

PROJECT 325B

TECHNICAL SUMMARY REPORT

PERIOD: May 1, 1972 to June 30, 1972

Submitted By:

[Redacted]

Project Manager

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SUMMARY OF SIX MONTH PROGRAM FROM
1 January 1972 to 1 July 1972 .

The objectives of this six month program were:

1. To determine the nature of shelf life/speed decay.
2. To determine the chemical mechanism of shelf life/speed decay as a logical prelude to solving the problem.
3. To determine the cause(s) of random nonuniformities in the photographic process.
4. To determine the specific purity levels required of the formula constituents to produce consistent results, batch-to-batch.
5. To work towards a shelf life of 60 days at 70°F with no loss of existing photographic properties.

For all practical purposes these objectives have been realized and as a result a logical program for solving the shelf life/speed decay problem has been defined (cf. Free Radical Camera Speed Film "Control of Shelf Life Mechanism"- Proposal, A Six Month Program, 1 July 1972 to 1 January, 1973).

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The objectives for this program were realized in terms of the following accomplishments:

1. The nature of shelf life/speed decay was determined, and has been discussed in prior reports (cf. January through April Monthly Summary Reports).
2. Two mechanisms of speed decay have been elucidated. The first is a physical process involving loss of the volatile activator, CBr_4 (cf. 1.2.1.2). The second is a chemical decay mechanism which involves autoxidation of D260 to form D260-hydroperoxide followed by its decomposition to 4DMP which is a powerful antioxidant and hence the direct cause of reduced sensitivity (cf. Figure 25). Various aspects of this mechanism have been discussed in prior reports and also Section 1.1.1.5 of this report.

3. Several causes of random nonuniformities have been identified. They are:
 - a) Irregularities and imperfections in the Mylar base (2.2.2.2)
 - b) Air-borne particulates (2.2.2.2)
 - c) Air-borne gaseous contamination (prior reports)
 - d) Poor solubility of D7 (1.10.1)
4. Specific purity levels for all ingredients have not as yet been defined. However, purification and handling procedures have been advanced to the stage where the desired batch-to-batch consistency with concurrent photographic reliability has been realized.
5. Significant improvement in shelf life/speed decay has been realized. This has been accomplished by overcoating with polyvinyl alcohol (PVA) to prevent loss of CBr_4 (2.2.2.2). The low permeability of PVA may also be retarding the autoxidation of D260. The use of distearyl thiodipropionate (DSTDP), a known peroxide/hydroperoxide decomposer, has also dramatically altered the speed decay behavior. The most significant aspects of these early improvements, however, are in providing strong supporting evidence for the postulated mechanisms of decay and in providing the most promising approaches to solving the problem.

1.0 CHEMICAL R and D

1.1 Leuco Dye Program

1.1.1 D260

1.1.1.1 Role of D260 in Speed Decay - Ingredient Interaction Decay Studies

In order to determine more fully the interaction taking place between D260 and D7, four solutions of the materials were prepared and allowed to stand in the dark at ambient temperature, at first without exclusion of oxygen.

Solution I:	D260, D7 (No reaction with benzene)	} Purified Benzene
Solution II:	D260, D7 (Reaction with benzene)	
Solution III:	D260, D7 (No reaction with benzene)	} Untreated Reagent Grade Benzene
Solution IV:	D260, D7 (Reaction with benzene)	

The purpose of this study was to determine not only the effect of interaction between D260 and D7 but what effect different grades of purity of D7 and benzene have on this interaction (cf. April Summary Report, Section 1.5.2, p.10).

Film results showed that there was some interaction taking place between D260 and D7 in solution. All four of the D260-D7 solutions (regardless of D7 or benzene used) were found to be photographically inert for all practical purposes on optical development after 9 days and completely dead after 11 days. The development times were found to increase (44 to 300 seconds), the fog levels increased to maximum density, and the Dnet decreased from 1.8-1.9 to 0 (see Figures 1 through 4).

A great difference was found, however, in the printout mode. After 11 days, the four solutions were found to give the same photographic results as when they were freshly prepared. The maximum densities and fog levels were identical; the shape of the curve, however, was found to be slightly different in that the shoulder slowly disappears after 11 days.

These results proved to be independent of the D7 or benzene used. It was subsequently discovered that the color change of D7 in benzene occurred with only one sample of D7, that one

which was in current use. Recrystallization removed an unidentified impurity which could be seen by TLC. The resulting D7 no longer showed the color change. This impurity does not appear responsible for speed decay, however, since the above results were observed with either D7.

In order to determine more fully the effect of oxygen on the various interactions taking place in solution, the following oxygen-free solutions were prepared:

Solution V:	D260	
Solution VI:	D260, 4PO	
Solution VII:	D260, D7	Polystyrene/Benzene
Solution VIII:	D260, 4PO, D7	

All the additives, including the polystyrene and benzene were degassed and stored under an argon atmosphere. After 25 days under oxygen-free conditions, the following results had been obtained:

Optical Development:

- 1) Sol. V - Dnet had decreased slightly; AEI speed had not changed; T_r had almost doubled.
- 2) Sol. VI - Dnet had not changed; AEI speed was constant; T_r had almost doubled.
- 3) Sol. VII - Dnet had decreased (approximately 20%); films were blotched (same results since $T_v = 7$ days); T_r had almost doubled.
- 4) Sol. VIII - Dnet had decreased (approximately 30%); films were blotched (same results since $T_v = 11$ days); T_r was up approximately 50%.

Printout Mode:

- 1) Sol. V - No change.
- 2) Sol. VI - No change; if anything, the maximum density and Dnet were becoming higher.

- 3) Sol. VII - Dmax and Dnet were decreasing (approximately 15%).
- 4) Sol. VIII - Dmax and Dnet were decreasing (approximately 15%).

In order to understand more fully the interaction taking place between D260 and CBr_4 , a solution of the two materials was made in the oxygen-free chamber. 4PO was added to an aliquot portion of the solution outside the chamber to complete the Formula 5 system and the resulting film evaluated in both modes. Optical development of a freshly coated film produced a completely fogged film with no image; printouts gave an almost normal Formula 5 film (maximum density 1.27) but for a higher blue fog (fog density 0.17). It would appear that some reaction is taking place in the oxygen-free atmosphere to explain this blue fog in a freshly coated film. The presence of 4PO is not only necessary to augment the image but also plays an important part (perhaps as a source of oxygen) in the stability of D260 in the presence of CBr_4 .

1.1.1.2 Purification of D260

During this period two shipments totaling about 900 g of D260 were received from ChemSampCo. Both shipments consisted of light blue material which was exceedingly clean by TLC, containing only a trace ($<0.001\%$) of D427, the anthrone.

Simple charcoal treatment of benzene solution removed practically all color from small samples of the first shipment. However, several experiments with charcoal alone and charcoal-alumina combination showed that a trace of green or blue color invariably remained. It was therefore decided that the initial purification to give white material would be by column chromatography over basic alumina, followed by recrystallization.

This purification procedure will now be considered the primary initial procedure for all D260 received from ChemSampCo provided the quality of the crude received remains constant as monitored by TLC.

This base photograde material is acceptable for continuation of film studies both by the chemistry team and the engineering. Further purification studies with this material will continue with the goal of ever superior D260. In concert with these

further refinements, mass spectral analyses will continue in an attempt to correlate key impurities with photographic response.

1.1.1.3 GC Analytical Studies

Formula 5/D7 coatings in benzene were examined by gas chromatography. Two components were sought: tetrabromoethylene and 4-picoline (4P).

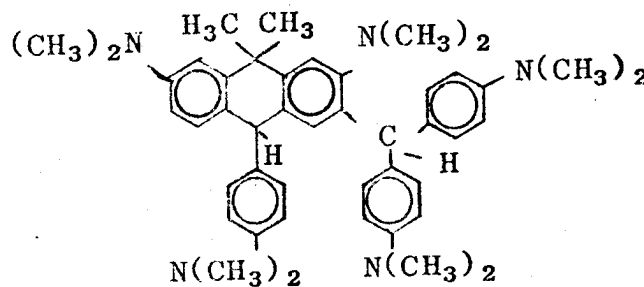
Tetrabromomethylene was found to be present at a level of 0.0009 mg/cm² in the film, but it is present as an impurity in the CBr₄ stock solution at about the same level.

In searching for 4P a peak eluting very close to 4P was identified as bromoform. 4P was finally resolved from bromoform by addition of 4P to the film extract. No 4P could be detected in the undoped film extract.

It has not yet been found possible to get D7 or D260 through the gas chromatograph using conventional techniques. Pyrograms are easily obtained but not much useful information could be obtained from pyrograms of film extracts. No further components have thus far been identified in film extracts. It seems likely that TLC is more promising in obtaining further information.

1.1.1.4 Mass Spectra

Analysis of mass spectral data of various samples of D260 has revealed a relatively large peak at M/e 666 in some samples. The 666 contaminant could be a condensation product of D260 and Michler's hydrol from D259 synthesis. Such a conceivable product could have the following structure (or isomer).



This M/e would in fact be 665 but it is quite possible that instrument error might account for this small difference.

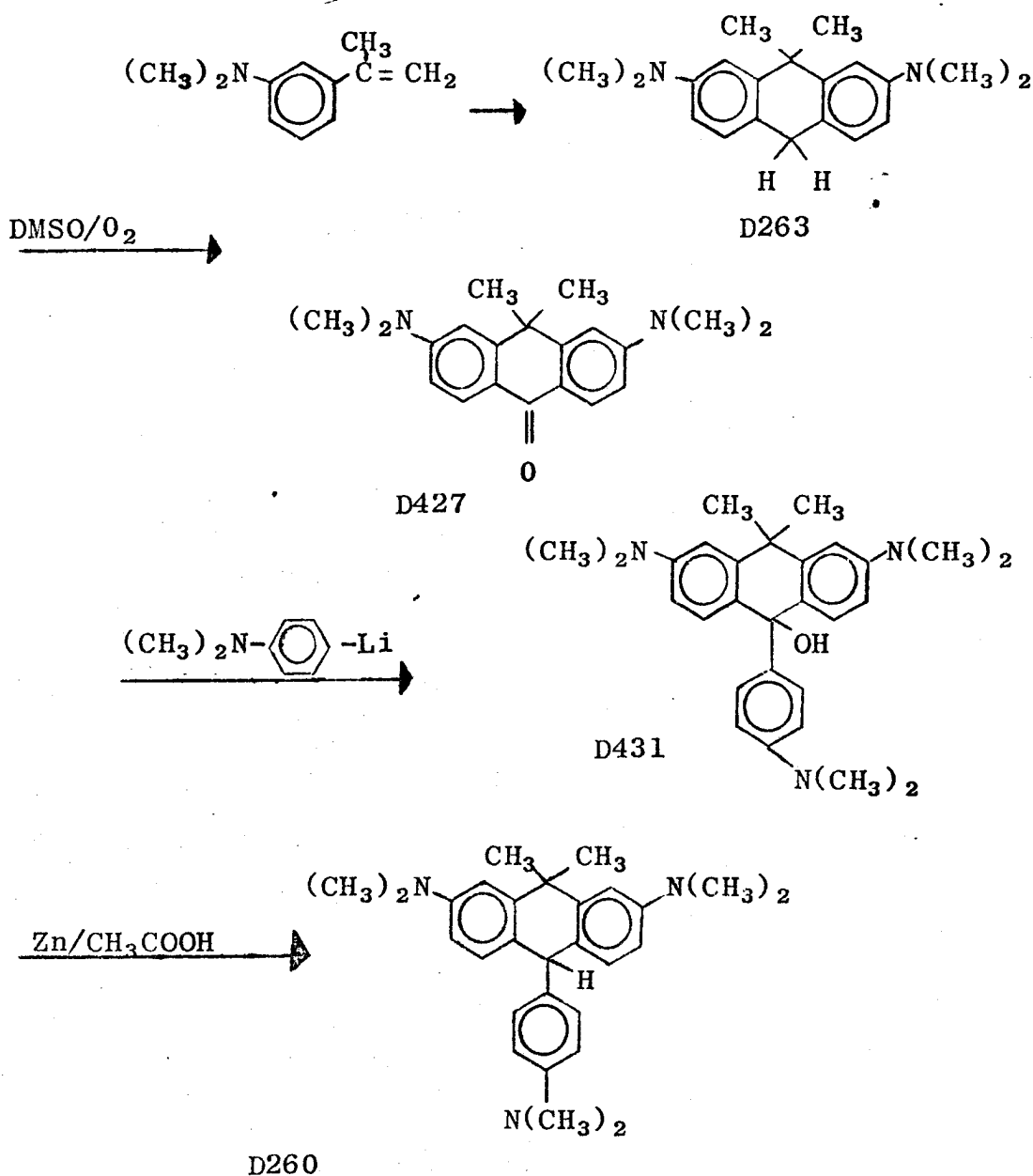
In these mass spectra of D260 showing the peak at 666 (or 665) this peak is invariably accompanied by an M/e of 134 and 253, nearly always varying in proportionate intensity. The M/e 253 is almost undoubtedly the carbonium ion from Michler's hydrol, the principal peak in most LCV analogs which have been analyzed.

1.1.1.5 Irradiation of D260 with UV

A sample of D260 was dissolved in benzene and placed in a quartz UV cell and irradiated with UV light. After 4 hours, p-dimethylaminophenol could be detected by TLC at a concentration of about 1/100%. The solution was diluted to a concentration of 1/100 that of the original. D427 (anthrone) was detected in this solution at a concentration of about 1/10,000% by TLC. From this it was concluded that the phenol and D427 were present in about equal concentrations. No difference was detected in the behavior between this experiment and one using acetone as a solvent. The equal concentrations of anthrone and 4DMAP are consistent with the hypothesis of their simultaneous formation from D260-hydroperoxide (see Figure 25).

1.1.1.6 Alternate Synthesis of D260 - The Anthrone Route

The alternate synthesis route to D260 starts with m-isopropenyldimethylaniline which is converted to D263. The latter is oxidized to the anthrone (D427) and reaction with p-lithiodimethylaniline yields D431, the carbinol of D260. D431 can be reduced to D260, the desired leuco.



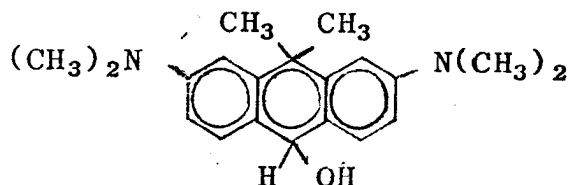
The reasons for pursuing this alternate route were to improve the yield of D260 from m-isopropenyldimethylaniline, to reduce the amount of tetramethylbenzidine contaminant in the crude D260, and to determine the relative photographic properties of the leuco prepared by another route.

1.1.1.6.1 Oxidation of D263 to D427 with Dimethylsulfoxide

The oxidation of D263 with DMSO and oxygen to a mixture of D427 and the corresponding anthranol was studied over a traverse of temperatures and reaction conditions. It proved to be the best route to D427 and superior to the "dismutation" originally reported in the literature (Ref. 1)..

The best sample of D427 by TLC was recrystallized from ethanol to give beautiful looking straw-yellow spiny needles, with, however, a broad melting point range. A less beautiful sample from recrystallization and charcoal was a light green solid, mp 209.8-212.4°C (lit. mp 207-8°, Ref. 1).

All D427 prepared by this oxidation route contained at least small quantities of the anthranol: 3,6-dimethylamino-10,10-dimethyl-9,10-dihydro-9-anthranol.



The anthranol and D427 appear together in many samples resulting from this oxidation and both fluoresce strongly under UV. The anthranol fluoresces from two to four times as much as D427, thus it can be detected at levels of 0.125 to 0.25 mg/liter.

Alternate oxidation procedures were not successful. Use of dicyclohexylcarbodiimide, Girard Reagent T, phenyl isocyanate, and potassium carbonate was not helpful.

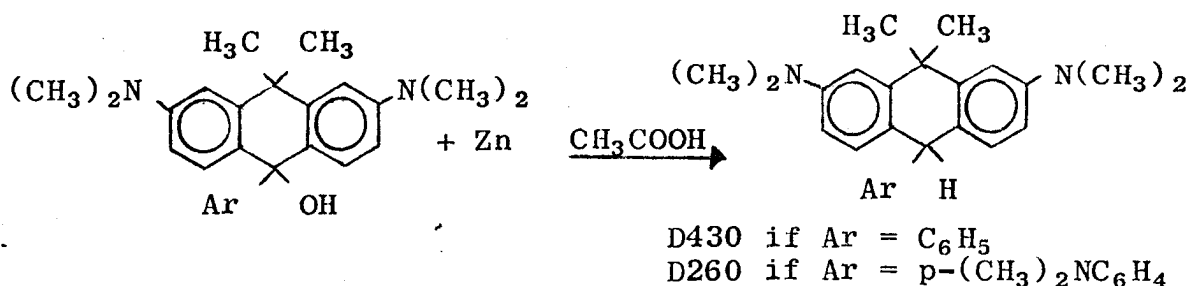
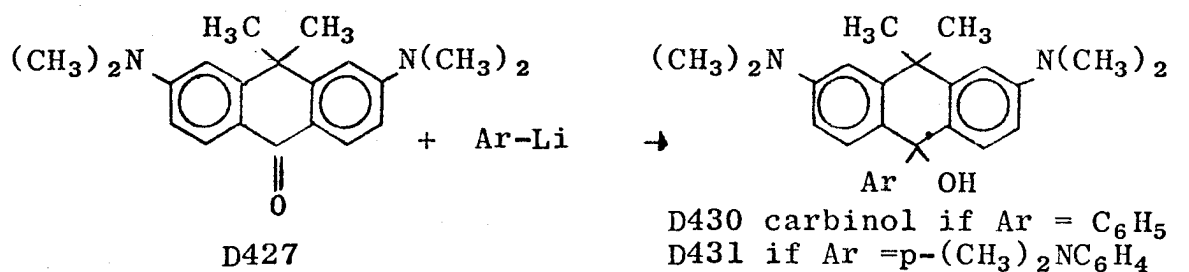
In another unsuccessful approach, D263 was treated with nitrous acid in the hope of preparing the oxime of D427.

1.1.1.6.2 Preparation of D431; Possibility of D263 Contaminant In Leucos

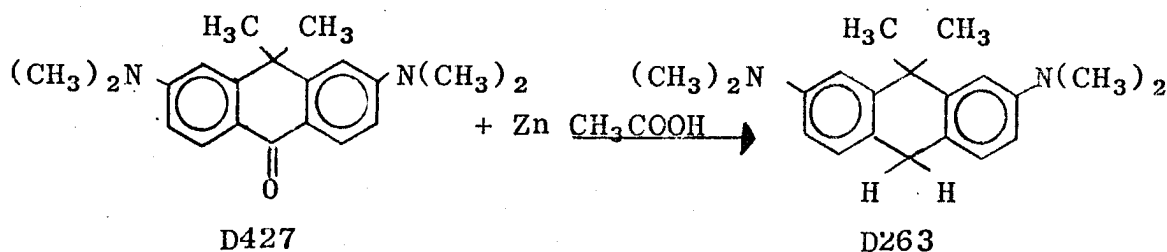
The reaction of D427 with p-lithiodimethylaniline to form D431 was not completed during this period.

It became obvious, however, that the optimum ratio of D427 and aryllithium would be a problem. The final leuco was almost certain to be contaminated with D263, itself very sensitive photographically and likely to distort the photographic evaluation of the leuco.

The Anthrone Route to leucos is exemplified by the proposed synthesis of D430 and D260:



Unreacted D427 is a specific disadvantage in carbinols such as the carbinol of D430 and the carbinol of D260 (D431), since subsequent reduction of the carbinol with zinc and acetic acid will reduce the D427 contaminant to D263. There is no question about D427 being reduced to D263 with zinc and acetic acid. It has been verified experimentally. The yield is high, perhaps quantitative.



If the intermediate carbinol is contaminated with either D263 or D427, the final leuco would have to be contaminated with D263.

Choosing the proper proportion of reactants for the organolithium reaction may be impossible, since using too much organolithium results in the reduction of D427 in the reaction mixture to D263, while excess unreacted D427 will be reduced to D263 when the carbinol product is reduced with zinc and acetic acid to the ultimate leuco.

As long as the proportion of D263 in the final leuco can be assayed, its presence may not be disabling. Preliminary evaluation of D263 as a leuco (reported in Section 1.1.1.7.1) indicates that it is very active photographically, but the improvement appears to be proportional to the quantity added.

Excess p-lithiodimethylaniline (in the D260 synthesis) will also result in generation of 4-dimethylaminophenol on subsequent hydrolysis. This phenol inhibits the photographic reaction and would have to be removed.

1.1.1.7 D260 Analogs: Other Leuco Anthracenes

1.1.1.7.1 D263: 2,7-Bis(dimethylamino)-9,10-dihydro-9,9-dimethylantracene

This compound has been investigated as a possible replacement for D260 as the leuco in the Formula 5 and 5/D7 systems. For its preparation:

A) Formula 5 - With optical development, D263 appears to be comparable to D260; if there is any difference it would be that D263 gives a slightly higher maximum density (1.00) than D260 (maximum density 0.63) at shorter development times (42 seconds as compared to 77 seconds). Speed decay (no photosensitivity after one hour) appears the same in both cases.

In the printout mode, D263 gives higher maximum density (1.62) than D260 (maximum density 1.47). Figure 5 shows a comparison of the printout curves obtained from D260 and D263. To show that this difference is real, addition of small amounts (1%, 5%) of D263 was added to a normal Formula 5 coating. The maximum density of the curve increases as the concentration of D263 increases. With respect to speed decay, their behaviors are comparable. Again if there is any difference it is that D263 aged films have higher maximum density than

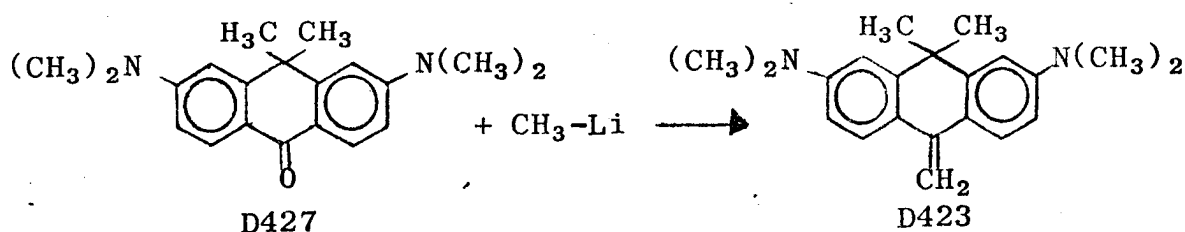
B) 5/D7 - With optical development, D263 was found to give slightly higher maximum density (2.22) and gamma (3.4) than the corresponding D260 (maximum density 2.17; gamma 2.4). Figure 6 illustrates the difference in curves obtained from D260 and D263. To show that this difference is real, again small amounts (1%, 5%) of D263 were added to a normal 5/D7 coating. The maximum density of the curve increases as the concentration of D263 increases. It is also interesting to notice that the gamma increases with no change in speed in the same manner. Perhaps D263 can be used not only to increase the maximum density but also to control the shape of the curve so that a film with a particular gamma can be obtained. Both materials appear to behave the same with respect to speed decay.

1.1.1.7.2 D430: 2,7-Bis(dimethylamino)-9,10-dihydro-9,9-dimethyl-10-phenylanthracene

Pure D430 carbinol has not yet been isolated from this reaction mixture.

1.1.1.7.3 D423: 2,7-Bis(dimethylamino)-9,10-dihydro-9,9-dimethyl-10-methyleneanthracene

Methyl lithium was reacted 2:1 with 3 g of D427 to yield 2.95 g of a pale yellow-white solid, crude mp 125-134°C. Recrystallization from 80% ethanol gave 2.45 g of a straw yellow-green solid, mp 144.4-146.2°C (lit. mp 144.5-146°C, Ref. 1).

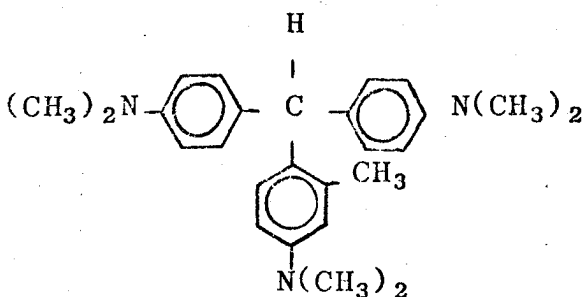


The D423 olefin is formed directly. The intermediate carbinol is not isolated.

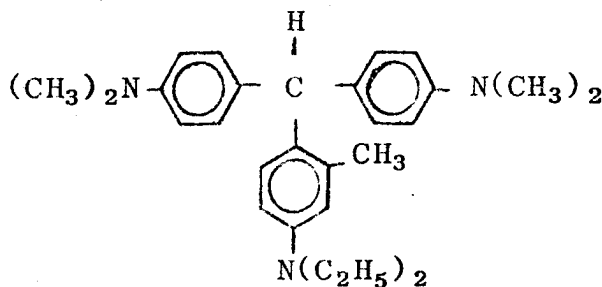
Presence or absence of D263 contamination in D423 is an important question, and cannot be answered at present. It is not possible to discern even 50% D263 in D423 in the TLC systems available at this writing. This material has not yet been evaluated photographically.

1.1.1.8 Other Leucos: D416, 2-Methyl LCV Homolog; and D420, 2,6-Dimethyl LCV

The current structure of D416 is probably α^4 , α^4 -bis(4-dimethylaminophenyl)-N,N-diethyl-3,4-xylylidine, a simple homolog of 2-methyl LCV.

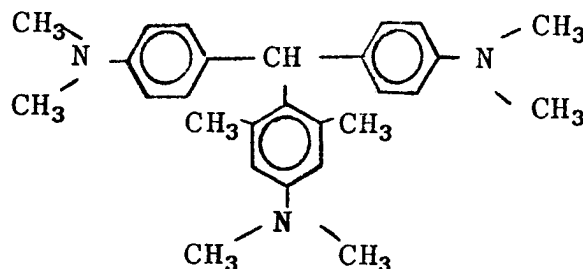


originally stated structure for D416



probable structure of D416

D420:



D416 and D420 were tested in the printout mode and gave some encouraging results. In the Formula 5 system, densities of 0.39 - 0.48 and fog levels of 0.06 - 0.07 were obtained; in the 5/D7 system, densities of 1.40 - 1.74 and a fog level of 0.08 were obtained.

In aging tests the two leuco dyes, D416 and D420, were compared to D260 and LCV using the printout mode ($T_e = 900$ seconds). D416 and D420 were found to lose greater dye density than do either D260 and LCV over a 24 hour period.

In view of these results it appears safe to assume that the poor speeds and densities exhibited by leuco malachite green (LMG) and its analogs (cf. April Summary Report, Section 1.1.2, p. 5) is a result of the third dimethylamino group being absent. The fact that none of the leuco crystal violet (LCV) analogs showed any improvement over LCV itself in regard to either speed or speed decay indicates that structural modifications of this nature will afford no advantage in overcoming the shelf life/speed decay problem. Therefore, any future work with leuco dye analogs will be restricted to the anthracene types represented by D260, D263, and D430.

1.1.1.9 Image Enhancers

1.1.1.9.1 D7

In order to prepare ultrapurified D7 a sample was recrystallized from pyridine-ligroin in the laboratory. It was then twice recrystallized from benzene in a glove-box under an argon atmosphere. The material was dried in a vacuum desiccator over K_2CO_3 in the glove-box and then transferred under vacuum to the film group.

1.1.1.9 .2 D8, 4-(p-Dimethylaminostyryl)quinoline

D8 was synthesized from redistilled lepidine (Adams Chemical Company, Round Lake, Illinois) and p-dimethylamino-benzaldehyde, using concentrated HCl as catalyst in a sealed pressure vessel at 130°C. The crude material was isolated by precipitation with water from a methanolic solution containing triethylamine. Recrystallization from pyridine-ligroin yielded 52.8 g (50%) of yellow needles mp 143.5 - 146°C.

For an ultrapurified sample of D8, 25 grams was recrystallized twice from benzene in a glove-box under an argon atmosphere.

1.2 Activators

1.2.1 Carbon Tetrabromide

1.2.1.1 Deterioration Studies

These studies were initiated in February, 1972. The various samples, stored both in contaminated air as well as in purified synthetic air (80% N₂, 20% O₂), remain intact and the evaluation will continue until a noticeable deterioration of any of the CBr₄'s take place. The testing procedure will be changed slightly so that the aging tests will be run every six to eight weeks. In view of the recently recognized synergism between CBr₄ and D260 (April Summary Report, Section 1.2, p. 6) it now appears unlikely that deterioration will be observed.

1.2.1.2 Loss of CBr₄: A Cause of Speed Decay

Once the loss of CBr₄ by sublimation was realized as a possible cause for at least part of the observed shelf life/speed decay problem, a means was sought for measuring the rate of loss of CBr₄ from film. The means was found in the visible absorption spectrum (Figure 23) of unexposed 5/D7. The weak absorption maximum at 630 nm was found to decrease with the age of the film according to curve b in Figure 24. Independently, films were formulated with lower concentrations of CBr₄ (1.0 equalling the standard formulation) and the absorption maximum at 630 nm was found to also decrease according to curve a. A noticeable loss in photosensitivity occurred with decreasing concentration of CBr₄, with a very significant loss

occurring below about one-half the normal concentration. Relationship of these two independently generated curves indicates that as much as 50% of the original CBr_4 film-concentration may be lost within the first two hours. This fact indicates that indeed loss of CBr_4 is a major factor in the observed speed decay.

Another independent means of measuring the loss of CBr_4 is being sought in order to substantiate and hopefully refine these data.

1.2.2 Other Activators

α,α,α -Tribromo-2,5-dimethylacetophenone (I) and hexabromodiacyetyl (II) have been studied as possible activators in the 5/D7 system. Both I (500 mg) and II (1.2 g) were used in place of CBr_4 and a traversal of 4PO (0 to 100 mg) was also carried out. In all instances, optical development resulted in total fog with no discernible image. Printouts of II also gave no image with a high fog level being produced (the fog density decreased as the concentration of 4PO was increased). Printouts of I gave significant image when no 4PO was present; the maximum density was 1.57 (fog density 0.26).

No further work is currently planned since there is no apparent advantage to be gained over CBr_4 .

1.3 Amine Oxides

1.3.1 Heteroaromatic N-Oxides

Since 4-picoline-n-oxide, 4PO, is presently used in the 5/D7 and 5/DPA systems, an extensive evaluation of heteroaromatic N-oxides was carried out. The following compounds in this class were evaluated:

N1	pyridine-N-oxide
N2	2-picoline-N-oxide
N3	3-picoline-N-oxide
N4	4-picoline-N-oxide (4PO)
N5	4-ethylpyridine-N-oxide

N6	4-ethyl-3-methylpyridine-N-oxide
N7	4-phenylpyridine-N-oxide
N8	benzo[f]quinoline-N-oxide
N9	benzo[h]quinoline-N-oxide
N10	4-methoxypyridine-N-oxide
N11	2-hydroxypyridine-N-oxide
N12	3-hydroxypyridine-N-oxide
N14	4-nitropyridine-N-oxide
N15	2,6-dichloropyridine-N-oxide
N16	8-hydroxyquinoline-N-oxide
N20	4,4'-azopyridine-1,1'-dioxide
N27	benzo[a]phenazine-12-oxide
N28	phenazine-N-oxide
N33	quinoline-N-oxide
N34	2,6-lutidine-N-oxide
N36	2,4-lutidine-N-oxide
N37	4-t-butylpyridine-N-oxide

Table 1 contains the photographic results of the tested aromatic N-oxides.

Since it has been shown that the absence of 4PO in the 5/D7 system gives very little image ($D_{net} = 0.11$) with a high red fog (1.29) (1756-26-1), finding the correct N-oxide to optimize the photosensitivity of the film is of the utmost importance. Previous results obtained with 4PO have also shown the importance of purity and drying over P_2O_5 to remove the final traces of water. The investigation included also the following points:

- 1) Effect of isomer position (2 and 3 vs. 4) of the picoline-N-oxide
- 2) Effect of substitution in the 4-position of the aromatic-N-oxide
- 3) Effect of any other substitution (mono- as well as di-) on the nucleus of the aromatic-N-oxide.

The materials were purified to the highest degree and compared favorably with literature values; materials which were of particular interest were sent for analysis. All the N-oxides were dried over phosphorous pentoxide and stored in a vacuum desiccator over the same drying agent until ready for use.

Of the picoline series, only the 4-substituted isomer gave the required maximum density (2.01) and acceptable fog levels (0.23); the 2- and 3-isomers gave very faint images ($D_{net} \approx 0.45$) with high fog levels (0.45 - 0.88).

Varying the substitution (hydrogen, ethyl, t-butyl, methoxy, phenyl and nitro) in the 4- position did not follow any pattern which could explain the photographic results. The 4-ethyl derivative behaved similarly to 4PO and gave a maximum density of 1.90 and a fog level of 0.28; the 4-t-butyl derivative gave a maximum density of 1.55 and a fog level of 0.28. In theory, these results should have been equal and if any difference were to be found, the t-butyl, because of its increased inductive effect, might have been expected to give higher Dnet value. The other derivatives gave either very faint images ($D_{net} \approx 0.31 - 0.40$) and high fog levels (0.40 - 0.75), or completely blotched films.

None of the other derivatives (mono- as well as di-substituted), save 4-ethyl-3-methylpyridine-N-oxide, (N6), gave any acceptable film results. N6 gave lower density (1.63) and normal fog level (0.26) at comparable equivalent weight of 4PO. When its concentration was cut to one-half, the maximum density increased to 2.00-2.26 and the fog level remained constant (0.27 - 0.20); increasing its concentration two fold gave comparable results. It would appear that this derivative is as good as 4PO and actually may be slightly better in that its concentration factor is apparently not as critical as 4PO.

1.3.2 Azoxyaryls and Other Amine Oxides

Since azoxy derivatives have the same functional group ($\text{>N}\rightarrow\text{O}$) that is found in N-oxides, the investigation also included various commercially available azoxyaryls. The following azoxyaryls were tested:

N17	4,4'-azoxyanisole
N18	4,4'-dichloroazoxybenzene
N19	4,4'-azoxyphenetole
N21	4,4'-azoxypyridine-N,N'-dioxide
N23	3,3'-dinitroazoxybenzene
N24	4,4'-dihexyloxyazoxybenzene

Solubility of the materials proved to be a major problem in coating, and no acceptable images could be obtained. Printout development produced faint images ($D_{net} \approx 0.16$) with high fog levels (0.30 - 0.68); optical development gave similar results.

Three N-oxides of alkaloids were tested:

N29	brucine-l9-oxide
N30	strychnine-l9-oxide
N31	tropine-N-oxide

Not only was solubility a problem in coating of the various alkaloids, N29, N30 and N31, but the materials were found to have no photosensitivity at all.

The aliphatic derivatives, N32 and N35, were also found to have no photosensitivity at all:

N32	N-methylmorpholine-N-oxide
N35	2,2'-(benzylimino)diethanol-N-oxide

1.3.3 Shelf Life and Speed Decay

Table 2 contains the results of the shelf life investigation of N-oxides.

From the data one can see that none of the N-oxides, except N5 and N6, were the equivalent of 4PO.

The pattern of speed decay of systems containing 4PO and 4-ethylpyridine-N-oxide (N5) was compared in the Formula 5 and 5/D7 systems at the normal equivalent weight for a standard control and at an increased level (90 mg/100 mg D260) using the printout mode of development (Te = 300 seconds). Figures 8 - 10 illustrate the results of this study.

In Formula 5 the big difference was found in the fog densities. N5 was found to give much higher fog levels (the higher the concentration of N5 the greater the fog density) than the corresponding values obtained by use of 4PO (increasing the concentration of 4PO had no effect upon the fog density).

In the 5/D7 system, lower Dnet values with higher fog levels are obtained. The loss in Dnet for either of the N-oxides at lower concentrations are equal over a 24 hour period; increasing the concentration to 90 mg/100 mg D260 resulted in a rather dramatic loss in Dnet for both N-oxides with N5 being affected more drastically. Again, the big difference in behavior between the two N-oxides was found in their fog densities. N5 was found to give much higher fog levels (the higher the concentration of N5 the greater the fog density) than the corresponding 4PO (increasing the concentration of 4PO had no effect upon the fog density).

1.3.4 Recommendation for Further Film Studies and Synthesis

4-Ethylpyridine-N-oxide (N5) and 4-ethyl-3-methylpyridine-N-oxide (N6) were the only materials that gave results similar

to 4PO. Since the results were at best comparable, no further work is planned at present. However, should the need arise to replace 4PO or if greater optimization of the 5/D7 system were necessary, N5 and N6 should be investigated to include the following studies:

- 1) Concentration traversal in the 5/D7 system
- 2) Solubility and purification comparisons to 4PO
- 3) More detailed shelf life study
- 4) Antioxidant addition study in the presence of the two materials
- 5) Studies in other photosensitivity systems; as Formula 5 and 5/DPA

In order to determine the effect of α -hydrogens on the methyl group in the 4-position of 4PO, 4-isopropylpyridine-N-oxide should be synthesized in order to complete the series of 4-methyl, 4-ethyl and 4-t-butyl derivatives.

2,4,6-Collidine-N-oxide is an example of a 4-alkyl-pyridine-N-oxide with two blocked ortho positions. It would be an interesting N-oxide to add to this plan. Synthesis should be simple and analogous to others we have recently run. Subject oxide will be scheduled for synthesis at the appropriate time.

1.3.5 Purification of 4PO

Practical grade 4PO was recrystallized from acetone-petroleum ether by the usual procedure. This white solid was then transferred to a LabConco glove box where it was recrystallized twice from benzene which had been pretreated by base and water washes and then stored over molecular sieve. The twice recrystallized 4PO was placed in a vacuum desiccator over P_2O_5 for two days.

1.4 Binder Studies

1.4.1 Pressure Chemical Polystyrene

All the viscosity and thickness measurements have been completed for the various polystyrenes (20.4, 110, 200, 390, 498, 670 and 2,000K) from Pressure Chemical. It has been determined that coating bars with a range of 0.3 mil to 3 mil will be required to give the necessary thickness comparable to that obtained from MX4500.

Five of the polystyrenes (110, 200, 390, 498, and 670K) were investigated by photographic tests in the Formula 5 and 5/D7 systems. The preliminary results indicate that there is no significant difference in any of the Pressure Chemical polystyrenes when compared to MX4500. The next photographic tests to be undertaken will be to determine the speed decay of Formula 5 and 5/D7 in the various Pressure Chemical polystyrenes.

1.5 Environmental Studies

1.5.1 Deoxygenation of Polystyrene

Samples of Styron 685 and Pressure Chemical 200K polystyrene have been successfully deoxygenated by successively purging with argon and evacuating to less than 0.05 mm at 220-240°C.

1.5.2 Purification of 4PO, D7 Under Controlled Conditions

The environmental chamber for final purification of materials under argon has been setup and necessary ancillary equipment made ready. Final purification have been completed (1.3.5 and 1.1.1.9.2).

1.6 Other Film Systems

1.6.1 The 5/DPA System

The extreme sensitivity of Formula 5/DPA with respect to D260 purity was demonstrated by initial studies comparing results obtained with formula 5/D7 with those using Formula 5/DPA. Although acceptable results in the formula 5/D7 system could be obtained, a poor quality film is obtained using Formula 5/DPA. This noticeable difference in behavior of these systems is again demonstrated when comparing effects of various additives on these two systems.

Addition of anthranol or various antioxidants, Plastanox 425 and distearyl thiodipropionate, controls the rate of reaction in the 5/DPA system so that an acceptable film can be obtained from a sample of D260 which previously had given poor results.

1.6.1.1 Reversal

During the initial screening of various samples of D260, a phenomenon which is referred to as a reversal was observed (Figure 11A). This phenomenon has samples of D260 purified with benzene/pet ether (Figure 11B) and has also been experimentally produced by the addition of either anthranol (Figure 11D) or antioxidants (Figure 11C) to the system. It appears now from both observed experimental results as well as from mass spectral curves obtained on various samples of D260, that either an optimum level of the impurity that is present in the D260 or the addition of antioxidants which have demonstrated the same capabilities as this impurity, can control the system so that acceptable results can be obtained.

Two experiments were run to verify the results which exhibit the reversal:

- 1) The amount of exposure received by the 8th step was calculated and a neutral density filter (2.0) was then placed over the stepwedge to reduce the first step exposure to that of the 8th step. This experiment produced the expected results in that the high density steps indeed moved up the wedge (Figure 12A).
- 2) The exposure time was then adjusted (from 15 to 4 seconds) so that the first step exposure would again be equal to that of the 8th step, after the initial exposure (4 seconds). The film was allowed to sit in the dark, before fixing, for the remainder of time of an ordinary printout (15 minutes). This experiment also produced expected results (Figure 12B).

For all experiments which were run on this system, a D260 which produces the uncontrolled reaction (originally considered bad D260) is being used as the control so that the effects of the additives can be more readily observed.

1.6.1.2 Formula Variations

1.6.1.2.1 4-Picoline-N-Oxide

The following levels of 4PO were tested in the Formula 5/DPA system: 10, 15 and 40 mg (per 4.5 cc coating). From this traversal it was determined that the present level of 20 mg was optimum for the work which is presently being carried out on this system.

1.6.1.2.2 Diphenylamine

Two levels of DPA (24 and 96 mg per 4.5 cc coating) were tested in the Formula 5/DPA system, in order to see if the same effects were observed now as were observed in the original traversal. It appears from these experiments that the 48 mg level is optimum.

1.6.1.2.3 Addition of D427/Anthranol

It was noted through the TLC work that samples of D260 which produced slower printouts and a controlled reaction contained small amounts of anthranol. Since a pure sample of anthranol was not available, a D427/anthanol mixture (80%/20%) was obtained and a traversal was run at the following levels: 1, 4, 10 and 17 mg (per 4.5 cc coating). Films obtained from this traversal exhibited a trend which appears to coincide with suspected results--a gradual decrease of the uncontrolled reaction was noted, and the reversal was observed in the transition. It appears that the reaction is affected by D427, at the 17 mg level, since a slight decrease in density was noted.

1.6.1.2.4 Addition of Dilauryl and Distearyl Thiodipropionate

The dilauryl and distearyl thiodipropionates were added to the Formula 5/DPA system in the amount which were found to be optimum for the Formula 5/D7 system (1.10.1.2). The results differed from those of the 5/D7 system in that while having no effect in the 5/D7 system (Figure 13) noticeable effects were observed in the 5/DPA system (Figure 14). The dilauryl derivative reduced image formation with no increase in density and the distearyl derivative increased image, image density, and background fog.

1.6.1.2.5 Addition of Michler's Hydrol

A traversal was run at the following levels: 2.25 µg, 22.5 µg, 67.5 µg, and 1 mg (per 4.5 cc coating), to see if the same effects were observed as with the anthranol. Results of these experiments show that although the reaction becomes controlled, a notable drop in speed and density is observed (Figure 15).

1.6.1.2.6 Addition of Plastanox 425

A traversal was run at the following levels: 100 µg, 225 µg, and 1 mg (per 4.5 cc coating), to observe the effects of an antioxidant on this system. Results of these experiments show that although the reaction becomes gradually controlled with no appreciable loss in sensitivity, the densities were still noticeably down (Figure 16).

1.7 Film Analysis of Decay Products

Nothing to report.

1.8 Dye Identification Program

1.8.1 Photolysis of Film Ingredients Excluding Binder

All of the ingredients except polystyrene in the proportions used for coating Formula 5/D7 were photolyzed for one hour six inches from a Sylvania 500 watt "Superflood" lamp, in two batches: with air bubbling through the flask, and with careful exclusion of air (nitrogen bubbled through the flask).

The visible spectra of the two photolysis runs were compared, Figure 17. They appear to show a different ratio between D260 dye and D7 dye, depending on whether air or nitrogen was bubbled through the photolysis reaction. The ratios are 2.46 in nitrogen and 1.29 in air. Presumably image is synthesized in the film under conditions of very restricted access to oxygen.

1.8.2 Dye Separation

Solid residue of mixed dyes from the photolysis of film ingredients in the absence of air (Section 1.8.1) (1852-43), was chromatographed on preparative silica plates, 2 mm x 20 cm x 20 cm.

Detail on the seven fractions is given in Table 3. The chromatograms show clear cut separation, so it is tempting to say that each of the seven bands reported upon in Table 3 is a separate component, in spite of the similarity of the colors of bands 2 and 3, and 5, 6 and 7.

This silica gel separation has been successfully transferred to analytical silica plates. Although there is some difference in details, the results generally parallel the preparative plate.

Results on the analytical plates are shown in Figure 18. Chromatogram 28 compares 5/D7 and 43 with five knowns: D7, D7 bromide, D7 dibromide, D260 and (old and impure) D392. Chromatogram 29 compares 5/D7 and 43 with other exposed films: Formula 5, 5/D7 without N4, 5/DPA and DPA/CBr₄. The reproductions in Figure 18 are approximately half scale. The best representation of the seven fractions from the preparative chromatogram is shown for 43 on Chromatogram 28 in the UV, where seven different spots can be distinguished.

Spots in the 5/DPA extract (Chromatogram 29) apparently can all be found in Formula 5 or in DPA/CBr₄, suggesting that in the 5/DPA system the diphenylamine may not be acting as an activator.

The objection to the silica gel system is that strongly polar solvents such as acetic acid must be used for elution. For this reason, work was begun on other substrates.

Work on alumina was instituted in order to be able to carry out the separation with solvents of lower polarity. Twelve components were found, seven of which were stronger than "faint."

Inert substrates were not useful in the separation of these dyes: cellulose plates ("Micro X," "Cellulose F") showed no resolution of the dyes with hydrocarbon eluents.

Chromatograms on Polyamide 6 gave a long tail which obscured the spots. This tailing was slightly reduced on Polyamide 11. Although improved, the resolution was still not good enough.

Further investment of time in inert substrates is not presently planned.

1.9 System Nonuniformities

Nothing to report.

1.10 Miscellaneous Studies

1.10.1 Formula 5/D7 Aging Studies

Coatings of the 5/D7 system were made and stored in the dark at ambient temperature to give some insight into the speed decay and fog buildup with respect to the following parameters:

- 1) Effect of filtering vs. unfiltering of the coating solution.
- 2) Effect of temperature on the background fog.
- 3) Effect of different storing procedures on the photosensitivity of the film.

Filtering the coating solution removes all undissolved D7, 4PO and D260 crystals and gives a film which looks better physically and removes a source of fog buildup (undissolved crystals of D7 seem to act as seeds for dye buildup).

Prior work has shown that if a freshly coated film is stored immediately at Dry Ice temperature, its sensitivity is not changed over an indefinite period of time. Since we speculate that a dark reaction is taking place at ambient temperature in the coated film, we are trying to determine what effect lowering the temperature has on this dark reaction and what effect it has on the film when the coated film is allowed to rise and finally stored at ambient temperature.

Aging studies of stored films show (printout mode) a definite decrease in net density and a continuing increase in fog level over 5 weeks. Films stored in air and light tight containers (I) have higher Dnet values and lower fog levels than the corresponding films stored in a drawer in the coating area (II). With optical development, the films were photographically inert after 24 hours. Increasing the exposure time (5 seconds at 24 hours, 25 seconds at 360 hours, and 60 seconds at 528 hours) gave net densities of less than 0.13 with a fog level about equal to that of the resulting maximum density. A point of interest is that none of the aged films showed any blotching phenomena at all.

A third set of films (III) was stored initially at Dry Ice temperature for 11 days and then allowed to age in the normal fashion at ambient temperature. Initial results have shown that the same aging pattern is being obtained for these films (printout and optical development) as had been obtained from films I and II. Evidently freezing the film at low temperatures preserves the photographic sensitivity and once the film is allowed to come to room temperature the normal path of speed decay is followed.

1.10.1.1 Formula 5 and 5/D7 Aging Study in Oxygen-Free Atmosphere

A) 5/D7 - An attempt to determine the speed decay of 5/D7 coating solution in an oxygen-free atmosphere proved fruitless in that reaction occurs as CBr_4 (Solution B) is added to the D260-D7-4PO mixture (Solution A). Optical development of the freshly prepared coating solution resulted in no image and complete fog (maximum density 2.55, fog density 2.55). Printout mode of development gave high maximum density (2.66) and high fog levels (fog density 0.57).

B) Formula 5 - With an exposure time of 0.09 seconds, optical development showed that the maximum life of the coating solution was 45 minutes (at $T_v = 0$, $D_{\text{net}} = 0.20$; at $T_v = 15$ minutes, $D_{\text{net}} = 0.15$; at $T_v = 45$ minutes, $D_{\text{net}} = 0$). With an increase of exposure time to 5 seconds, the D_{net} was 0.50 at $T_v = 90$ minutes and 0.45 at $T_v = 18$ hours.

Printout mode of development showed that the photosensitivity of the solution had not changed too greatly in a period of 18 hours (at $T_v = 0$, $D_{\text{net}} = 1.23$; at $T_v = 18$ hours, $D_{\text{net}} = 0.06$). However, there was a definite gradual buildup visually in the fog levels as the solution was allowed to age (at $T_v = 0$, $D_{\text{fog}} = 0.07$; at $T_v = 45$ minutes, $D_{\text{fog}} = 0.08$; at $T_v = 90$ minutes, $D_{\text{fog}} = 0.11$; at $T_v = 18$ hours, $D_{\text{fog}} = 0.19$).

Addition of D7 to the coating solution aged ($T_v = 18$ hours) in an oxygen-free atmosphere resulted in a completely fogged film with a slight image perceptible with optical development; printouts gave a normal 5/D7 film (maximum density 2.51) with a higher than normal blue fog background (fog density 0.17).

1.10.1.2 Addition of Antioxidants to Improve Shelf Life

Five antioxidants were added to the 5/D7 film to determine what effect they would have on the shelf life of the photo-sensitive system. The following aging studies were run.

Normal 5/D7 system plus:

- 1) Triethyl phosphite (TEP)
- 2) Triphenyl phosphite (TPP)
- 3) Plastanox 425 (P425)
- 4) Triethyl phosphite and Plastanox 425
- 5) Triphenyl phosphite and Plastanox 425
- 6) Dilauryl Thiodipropionate (DLTP)
- 7) Distearyl Thiodipropionate (DSTP)
- 8) Dilauryl Thiodipropionate and Plastanox 425
- 9) Distearyl Thiodipropionate and Plastanox 425

DSTP aids the shelf life for up to 20 hours. DSTP or DLTP behave similarly upon further storage: both materials have no effect upon speed decay after 20 hours in the printout mode and show no effect after one hour with optical development.

The distearyl derivative shows some promise and further work will be planned in the near future using the derivative in controlled aging tests.

All the other antioxidants had no effect on speed decay in that the speed loss of the films containing the materials was identical to a standard control film.

Optical development of DSTP behaves similarly to a normal control film upon aging ($T_v = 1, 21, 48$ hours); however, a marked difference was noted in the printout mode. Whereas the Dnet densities of the normal control film was down at $T_v = 2.5$ hours (1.76), 20 hours (1.00) and 96 hours (0.70), the values of the DSTP were found to be at $T_v = 2.5$ hours (2.43), 20 hours (1.96) and 96 hours (0.61). It would appear that the material is initially aiding the shelf life (20 hours) of the film and then completely loses whatever effect it has on the speed decay upon further storage. Further aging tests are still being run on the material.

For comparison of the effects of DSTP and DLTP in the 5/DPA system, compare Section 1.6.1.2.4., regarding Plastanox, see Section 1.6.1.2.6.

1.10.1.3 Addition of 4-Dimethylaminophenol and D427 to the 5/D7 System

In order to determine if 4-dimethylaminophenol (4DMAP) and D427 (anthrone), possible decay products of D260, are responsible for the loss in photographic sensitivity of the 5/D7 system, the materials were added to a freshly coated film and its photographic sensitivity compared to a standard 5/D7 film which was allowed to age for a period of 48 hours. It was hoped that addition of 4DMAP to a freshly coated film would affect the sensitivity by printout mode of development in the same manner as it would affect it by optical development.

Figure 19 illustrates an aging study of a normal 5/D7 film by printout mode of development ($T_e = 300$ seconds) over a period of 48 hours.

Figure 20 illustrates an aging study of a normal 5/D7 film by optical development ($T_e = 5$ seconds) over a period of 48 hours.

Figure 21 illustrates a freshly coated film containing 4DMAP and D427 and developed in the printout mode ($T_e = 300$ seconds).

Figure 22 illustrates a freshly coated film containing 4DMAP and D427 and optically developed ($T_e = 5$ seconds).

In the printout mode (Figure 21), addition of 20 - 30 μg of 4DMAP to a freshly coated film closely approximates the curve of a film which has been allowed to age for 3 hours. Addition of equivalent amount of D427 to the 4DMAP containing freshly coated film has no further deleterious effect on the shape of the curve.

With optical development (Figure 22) addition of 20 - 30 μg of 4DMAP to a freshly coated film does not approximate a normal 5/D7 control which has been allowed to age for a given period of time. The D_{max} 's were found to be identical but the fog densities were found to increase as the concentration of 4DMAP was increased. Addition of equivalent amount of D427 to the 4DMAP-containing freshly coated film appears to have no effect on the shape of the curve save for a slight shift.

Again, we appear to find further difference in the reaction mechanism taking place during the printout mode of development versus optical development. Perhaps the differences reside in the two different decay mechanisms. Future studies will involve attempts to relate these two mechanisms to observed decay patterns.

1.10.1.4 Addition of Diphenylamine to the 5/D7 System

The maximum amount of diphenylamine (DPA) that can be added to the 5/D7 system without changing its photosensitivity is 1.125 mg per 100 mg of D260. Increasing the amount (1, 10 mg) results in higher fog levels (0.46, 0.50) with optical development; printouts give the normal fog level (fog density 0.06) but decreased maximum density (2.37, 1.92). Addition of this material has no effect of the speed decay.

Since 4-dimethylaminophenol (4DMAP) was found to have a positive influence on the 5/DPA system, it was hoped that slight addition of this material to the 5/D7 system with DPA added would produce the same effect. This did not appear to be the case, however, in that addition of 22.5 μ g of 4DMAP in the presence of 1.125 mg DPA resulted in higher fog levels (fog density 0.37) with optical development and lower maximum density (2.23) by the printout mode. Speed decay of the 5/D7 system was not affected by addition of this mixture.

1.10.2 Formula 5 Aging Studies: Addition of Antioxidants to Improve Shelf Life in Formula 5 Systems

A 4PO traversal (0, 22.5, 45 and 90 mg) was run in the Formula 5 system to which were added the following antioxidants at the given concentrations:

- 1) Plastanox 425, 450 μ g
- 2) 2,4-di-tert-amylphenol, 450 and 225 μ g
- 3) 2,6-di-tert-butylphenol, 450 μ g
- 4) Plastanox 2246, 450 μ g
- 5) Distearyl Thiodipropionate, 5.6 mg

The optimum concentration of 4PO that gives the greatest sensitivity to the system is 22.5 mg. Absence of the material gives no image (only blue fog and background) upon optical development; printouts give lower maximum density (0.9 to 1.0) and higher fog levels (0.20 to 0.30). Increasing the amount to 90 mg gives trace image (maximum density 0.19) and a slight blue fog (fog density 0.16); printouts remain unchanged (maximum density 1.20; fog density 0.07). The optimum sensitivity of the Formula 5 system containing the various antioxidants are:

- 1) Optical Development: maximum density, 0.40 to 0.50, fog density .20 to .30.
- 2) Printout Mode: maximum density 1.2 to 1.3, fog density 0.06 to 0.07.

With respect to shelf life, distearyl thiodipropionate was the only material that had any effect on the speed decay of the film. The material was found to impart some stability to the film over a short period of time (one hour with optical development, 3 hours with the printout mode).

2.0 ENGINEERING

2.1 Calibration and Maintenance

The equipment used by both the Chemistry and Engineering groups on Project 325B requires careful calibration and periodic maintenance to insure accuracy and reliability. All sensitometers, densitometers, red light development units and spectral sensitometers continue to be checked and cross correlated on a regular basis.

2.2 Shelf Life/Speed Decay

This area as approached by the Engineering group was broken down into three separate sections: 1) identification of the normal speed decay curve, 2) reactivation of aged films, and 3) overcoating as a means to prevent speed decay.

Before any attempt was made to alter the shelf life speed decay curve a thorough study was made of the speed decay curve associated with the Formula 5/D7 film system. The data generated in this study has yielded the speed loss vs. time (normal decay curve shown in Figure 26). This curve shows that an amplification factor of 8,000 at 0 hours has decreased to a factor of only 30 after 10 hours. With this data as a baseline it was possible to proceed to work on reactivating aged films.

2.2.1 Reactivation

Of the several methods of reactivation possible the most likely to succeed seemed to be, either film storage in CBr_4 vapors, treatment with benzene vapors of the sensitive layer before exposure or some combination of both.

Samples stored in a container with high CBr_4 vapor concentrations for periods of up to 10 hours showed considerable improvement over the standard decay curves. This data is shown in Figure 26, Curve 2. For storage times greater than 10 hours the samples degraded rather severely.

The same was also true of samples stored in a normal room environment and then treated with benzene vapors for periods of time ranging from 30 seconds to 5 minutes. For sample storage times of up to 20 hours there was a considerable improvement due to the benzene treatment just prior to exposure as seen in Figure 26, Curve 3. However, beyond that time there was again a rapid speed loss.

Some additional work was done utilizing a combination of these techniques; however, the equipment refinements and the quantity of samples needed to truly define the area dictated that this work be continued at a later date.

2.2.2 Overcoating

Since a relationship appeared to exist between the loss of both benzene and CBr_4 the entrapment of both these chemicals in the sensitive layer was possible by overcoating with a polyvinyl alcohol (PVA) and H_2O solution.

The effect of the PVA overcoat was dramatic and immediate. Printout speeds increased from 1×10^{-4} to as high as 2×10^{-1} AEI in some instances. This must be considered the result of the exclusion of oxygen from the sensitive layer by the oxygen impermeable PVA layer. The exclusion of oxygen also has the affect of allowing the exposed areas to build up in density during the interval between exposure and processing. This procedure of exposure, delay and then processing has yielded direct printout speeds of 0.2 AEI and the maximum has most certainly not been realized. Without the PVA overcoat the printout AEI speeds are 1×10^{-4} .

Removal of the 0.5 mil PVA layer is accomplished by washing the sample in a water bath. Though the nominal thickness of this layer is about 0.5 mil, complete protection has been attained with a layer as thin as 0.1 mil. The film is then treated with fix solution in the final step of the processing.

One problem was encountered due to the exclusion of oxygen. After coating, small "sites" soon began to grow into larger spots which finally covered the entire film sample. The initial severity of this problem was such that film samples were unable to be stored in the overcoated condition for more than 15 minutes.

This condition has been identified as having any of several causes. The most directly responsible was found to be any and all forms of particulate matter in the air, on coating plates in solutions, etc. Pressure sites caused by the shearing action on the cutting board and by the overcoating draw bar contributed to this problem. These conditions can be eliminated by either dip or spray overcoating the individual samples. Irregularities on the coating plate have been eliminated by the use of an optically flat glass (8" x 8" x 1/4") coating plate mounted in a vacuum frame.

The fact that irregularities and imperfections in the Mylar base are also responsible for some of the spot growth has been demonstrated by coating and then overcoating the standard chemical solutions on an optically flat glass plate. The number and size of these spots was thereby considerably reduced.

Particulate matter in the air has been reduced significantly by the use of Micro-void hoods surrounding the coating and weighing stations.

A parameter which has a marked effect on the spot growth is the time delay before overcoating. The minimum drying time (approximately 2 minutes) before overcoating is optimum since maximum photographic speeds are attained. Under ideal conditions samples can now be stored for periods of up to 48 hours at 70°F without complete spot overgrowth as opposed to the original limit of 15 minutes.

Figure 27 shows the relative speed loss for direct print-out samples overcoated with PVA compared to the non-overcoated control. The overcoated samples are in all cases faster than the non-overcoated controls and they also show a marked improvement in the slope of the speed loss curve. The only limiting factor preventing the collection of data points beyond 48 hours room storage is the growth of the spots previously described.

The samples overcoated with a 30 or 60 minute delay after coating the sensitized layer are able to be held for periods longer than 40 hours but are not capable of red lite development and do not approach the initial speeds of a sample overcoated after a 2 to 5 minute drying time.

Overcoated samples have also been red lite developed with the PVA in place. Samples with AEI's of 1.0 have been produced

in this fashion although no effort has been made to attain maximum speeds. It also appears that the PVA layer can be removed and the sample then treated as a normal non-overcoated sample; however, data on this subject is not complete.

The effort on overcoating studies has been for consistency in coating and processing. This consistency is demonstrated in Figure 28. A normal red lite development (RLD) decay curve is shown with data for an overcoated series stored at 70°F and also another series at 44°F superimposed upon it. The remarkable aspect of this series is that while the normal RLD speed decay curve represents a maximizing of the processing conditions (namely RLD), the overcoated samples were all red lite developed the same length of time at each of the data points.

The samples stored at 44°F showed no apparent tendency for spot growth; however, the samples stored at 70°F in this series suffered from spot growth and were limited to only 48 hours. There was no speed loss at that point in time.

The following table shows the speed attained at various points in time under the conditions stated:

	0 Hours	24 Hours	48 Hours	360 Hours
<hr/>				
Normal				
No Overcoat, 70°F				
RLD	1×10^0	3×10^{-4}	1×10^{-5}	-
DPO	1×10^{-4}	2×10^{-5}	1×10^{-5}	-
Overcoat; 70°F				-
RLD	2×10^{-1}	-	3×10^{-2}	-
DPO	3.76×10^{-3}	1.25×10^{-3}	6.3×10^{-4}	
Overcoat; 44°F				
DPO	6.6×10^{-3}	4×10^{-3}	2.0×10^{-3}	2.0×10^{-3}

The characteristic curves for typical overcoated samples are shown in Figure 29. They are not dissimilar from the nonovercoated samples except that the printouts typically have a somewhat higher γ (1.8) and the red lite developed samples a γ slightly lower than normal (1.4).

Image evaluation of the Formula 5/D7 film system with the PVA overcoat was limited to red lite developed resolution targets exposed on the HIM-2 Microcamera. Figure 30 shows the previous AIM curve generated on this film and point X designates the data point using a 6.3:1 medium contrast target on samples processed to an AEI greater than 0.2. This data indicates there has probably been no significant movement of the AIM curve for a single overcoat in place through red lite development.

3.0 PERKIN ELMER INTERFACE, QC/QA

3.1 Perkin Elmer Interface

For the last six months [redacted] 25X1
provided the necessary film, supplies, equipment and technology for P.E. to conduct the 325B support contract. In the past P.E. support has included extended temporary assignment of their personnel at [redacted] to help design photo equipment and perform film evaluations. For the first time it has been possible 25X1
to send the 325B high performance film to an outside facility for extended lab studies. In the past only the physical properties of the film were measured at their lab. During the last six months sensitized, unexposed film was available for P.E. to expose and process at their facility. From the onset of the last six month contract period reasonable speeds were achieved at their laboratory. Because of the experimental nature of the film and the necessary use of hand coatings this achievement has been a considerable milestone.

A major portion of the last six months had to be expended to establish real comparability with [redacted] data, and to work out satisfactory production, shipping and contamination control techniques. The switching of P.E. personnel halfway through the 325B contract period required additional familiarization time. A considerable investment has been made, therefore, to establish another laboratory capable of producing data useful to the current 325B effort. The next six months should see considerably more data and studies produced by P.E. that will be directly useful to the 325 shelf life effort. Two consultants were hired by the customer via P.E. and were introduced to free radical film technology by P.E. The consultants should bear fruit in the coming six month contract period. 25X1

3.1.1 Support to P. E.

A total of ten film shipments were made to P.E. The program was started in the middle of January with the first shipment of film, solvent rinse and a red lite developing (RLD) unit. The last film shipment was made the middle of May. A total of ninety usable sheets, 7" x 7", were delivered. A large percent of the first four shipments had fogged in storage. The latter half of the shipments were of sufficient quality and quantity to maintain a laboratory effort by one man full time. The standard Formula

[REDACTED]

5/D7 coating without overcoat was used. The 7" x 7" Mylar sheets were approximately 40 to 60% covered. The shipment of the fix solvent was straight-forward and presented no problems. The delivery of the red lite unit required more care because of the importance of establishing comparability between the unit loaned to them and the identical units being used at [REDACTED] The development units are now comparable within the limits of the hand coated film. Because of the easy interchangeability of red light cut-on filters, the unit has been usable for some of their preliminary red lite studies. 25X1

3.1.2 Cross Calibrations

It took considerably more time than originally expected to establish comparability in data. Comparability has been established and the similarities and differences are real. The similarities are especially evident in the printout mode (See Figure 31 and Table 8). The differences in the RLD mode are considerable. The reasons for it and the solutions to the poor performance at their facility must be established early in the coming contract period. A very cursory search for the cause of the difference was made by duplicating the shipment and exact P.E. procedure [REDACTED] with the aid of the P.E. lab investigator. Because of the lack of separate manpower and facilities for the interface program [REDACTED], only a few tests were possible and the conclusions are not based well enough in fact to report. A separate, fully equipped dark room and a full time technician will facilitate the QC/QA and Interface effort for the next 1/2 year. 25X1 25X1

To facilitate cross calibrations the shipments include halves of a few control samples that are made routinely with the production of the film shipment. Because of the different nature of the free radical film compared to silver film, warning must be given to people who try to read the reports without giving sufficient attention to the cross calibrations. This area certainly will require more attention when the time comes for other facilities to be called on to expose and process 325 film.

3.1.3 Evaluation of Production, Shipping, Contamination

A successful procedure has been worked out for production and shipping although the knowledge of why the current packaging system really works has not been established. The work will continue on the assumption that this will be a satisfactory technique. The individual wrapping, dry ice freezing and double

bagging apparently prevents the fogging on long-term storage. The contamination level of the air at the P.E. facility apparently is satisfactory. The three sets of air samples taken there correlate with the moderately good air samples taken [redacted]. Again, the assumption will be made that no problem will arise in the next six months.

25X1

3.1.4 Monitoring of Results and Participation in Test Plans

Frequent communication and trips established close cooperation. The changing of personnel in March did change the specific tasks that were being planned at that point. The contribution made by P.E. to the [redacted] shelf life problem was the first curve showing shelf life of the printout mode. Shelf life of the latent image has also been done. The printout shelf life curve (see Figure 32) agrees well with the data previously taken by the Chemistry group and subsequently reproduced by the Engineering group at [redacted]. Except for some technology gained in the production and shipping of the film there has been no additional impact of the P.E. support program to the 325 shelf life problem. Within the next six months there will be considerably more value to their support on this problem.

25X1

25X1

3.2 QC/QA

QC/QA plays a major part; in assuring photograde material on a consistent basis, in the investigation and determination of the causes of the random nonuniformities, in the establishment of specific purity levels and the implementation of the syntheses procedures to produce these repeatably, and in the establishment of standards for coating rooms and coating procedures, and in the photosystem measurements that assured the past performance objectives which have been met are maintained as the shelf life problem is investigated.

The modus operandi has been primarily by monitoring the work of other groups, and when appropriate by performing independent tests. As the technology evolved, new standards were formulated in the materials, equipment and procedure areas which was especially important with the increase in number and diversity of coating groups. The QC function extended logically into the setting up of the P.E. laboratory. The quality standards that have been established for materials, particularly D260, have now been applied to the subcontractor and for receiving inspection. The analytic techniques useful for QC of photograde materials still requires work since actual film tests are still overly necessary for qualification of the material.

As the quality and quantity of materials have improved, the basic nature of the present photosystem formulation is becoming more evident in the sense that the characteristic curves are becoming more precise and repeatable. As the typical speeds and Dmax's increased the gamma has also increased. Higher gammas have been reported by the P.E. interface people, but for another reason. The high gamma is not considered a serious problem at this point because of the demonstrated system techniques, as well as chemistry techniques for lowering γ with essentially no compromise of other parameters. The overcoating technique has demonstrated a reversal in the gammas associated with the printout and the RLD mode. When the film R and D proceeds to a more final formula in coating technique, demonstration of the control of the gamma will then be appropriate.

The quantities of photograde material have been such that in the last six months' contract period there have been no "film failures." There has always been sufficient quantities of photograde materials that a fully sustained effort by the hand coating people was possible (See Table 4). Although quantities in the beginning of the last contract period were marginal, the estab-

lished lead times were included in the planning to prevent any shortage. At the end of the contract period the quantities were exceptionally good. Under the "Photograde on Hand Column," the quantities available 31 December 1971 are in parenthesis. In terms of "Photograde on Hand in Equivalent Coatings" our position appears especially good because only 200 equivalent coatings are necessary to sustain a full effort by the four coating people for one week. Because of the increased number of coating people and an increase in their efficiency planned for the follow-on contract period the margin is not excessive. The only material to show a decrease is the D7. The decrease resulted from the fact that one large batch was made approximately one year ago which has been sufficient to supply the project for the last year and still have a suitable amount remaining. In case of an accidental loss of photograde quality materials on hand the lead times have been worked out sufficiently well that no more than the listed number of days would be lost in resupply because of the maintenance of a crude/starting materials supply. /

Outside sources for supply of crude have been investigated. The critical D260 can now be supplied with satisfactory quality by ChemSampCo. QC/QA made an inspection visit last December which established ChemSampCo's size and type of operation and devotion to producing D260. Now that the synthesis operation has been worked out with the aid of the Synthesis Group Leader, they are a highly qualified source for D260 crude for the present contracted quantity levels. Since pilot plant operations for ChemSampCo, Columbus, Ohio, would be stretching their capabilities, another source such as Arapahoe, Boulder, Colorado, will be solicited when 325 film reaches the machine coating stage. The problems experienced in bringing the quality of ChemSampCo's material up to standard probably will be experienced by a new supplier, which means sufficient time (months) must be allowed for when the project expands to the pilot coating phase. The final purification of D260 is maintained at to prevent giving away 25X1 the state-of-art of the basic film system ingredient.

Several sources for CBr_4 crude have been found. The Freeman product continues to be used for the sake of consistency of laboratory data. Berk Int., which supplies a French product is superior and is of photograde quality as received, although purification is necessary for best quality. A domestic source for photograde CBr_4 will be assured when sufficient demand warrants. The final purification of CBr_4 is not an involved state of art as is the case of D260.

A balance sheet of the quantities of D260 (See Table 5) for

the past six months illustrates quantity control. Of the 5 kg to be delivered by ChemSampCo., 3200 g were delivered in the past six months and charged to 325B. Thirteen hundred grams remain to be delivered and will be charged to the proposed contract. Some of the earlier crude deliveries have been stored unused because better material came along before they were needed. The average purification yield is now 70% compared to the earlier 30%. Of the total 770 g of photograde material accepted, about one-third of that has been consumed and two-thirds of that is now on hand to start the follow-on contract effort. Table 5 lists the breakdown of the 255 g of photograde material consumed.

Tables 6 and 7 indicate the status of QC tests for the four principal ingredients of the 5/D7 formula. The considerable effort made to improve the quality and consistency of D260 material has yielded dramatic results the last six months. The existence of the contaminants TMB, anthrone of D260, DMAP, and their photo effects have been established. QC tests for these contaminants have been worked out, although the levels being measured are so low that they have not yet been determined with accuracy. Thin layer chromatography techniques are used in all three cases. They are sufficiently good for establishing the maximum quantity of contaminant allowable. A TLC plus UV illumination test for the anthrone can identify quantities as low as 10 ppb, which is now the upper limit for photograde quality. The test for DMAP is actually the test for the anthrone. The two have been proven to be present in equivalent amounts. Additional work will continue in identifying the condensation product, which is possible, and others. Purification, which eliminates the above contaminants apparently yields 70% or better. It is a two step process using dry column chromatography followed by recrystallization.

D7 contains only trace impurities after the first recrystallization. No apparent deleterious effect has been associated with this, therefore, no identification has been attempted. This may change as the quality of D260 and other materials, coating procedures, air contaminants, etc., are brought to higher standards. Four-Picoline-N-Oxide (4PO) also only contains trace impurities in crude which have shown no consistent deleterious affect, therefore, no identification was attempted. Purification requires only a straight forward crystallization and three days of drying. Since the material is highly hygroscopic, and because it is important for the photo system that it be extremely dry, the drying process requires particular attention. The CBr_4 contaminant, hexabromoethane, has been known. The effect probably

depends on the grade of D260. A TLC/D260 spray test will identify the contaminant. Purification can be accomplished by recrystallization or sublimation.

Quality control of the laboratory air has been determined to be especially important. Contaminants in the air can degrade the film if they are brought into the system during materials workup, film formulation, coating, or exposure and developing. Some contaminants have been tentatively identified with even more tentative acceptable concentration levels (See the table below).

STATUS OF QC FOR LAB AIR

Standards

Oxidants	30 μ g	O ₃ /Meter ³
HBr	9 μ g	Br ⁻ /M ³
HCl (?)	60 μ g	Cl ⁻ /M ³
Particulates:	Class 100 Preferably	
Temperature:	68 to 75°F	
Relative Humidity:	30 to 50%	

A six week series of two hundred air sampling tests established the probabilities that oxidants, and in particular HBr and possibly HCl, are contaminants at the microgram/cubic meter level. At these levels the pollutants in typical city air are sufficient to poison 325B film. Particulates also are a problem, although they may be functioning as a carrier for the gaseous contaminants. The temperature, 69° to 75°F, and relative humidity, 30 to 50%, guidelines are relatively broad, although necessary. These standards probably will have to be tightened with the progress in the 325B technology.

The tests that led to identification of these standards are as follows:

- 1) Air samples/frequency plots.
- 2) Charcoal filter analysis.
- 3) Film tests

- No dark fog when stored in clean air
- Purge with "clean" bottled gas
- Car exhaust poison test

- 4) Corroboration with known solution contaminant--acid
- 5) Particulate filter analyses
- 6) "Spots"

The charcoal filter analyses and the known contaminants for solution storage of the components corroborate the air sampling tests results. The importance of cleaning the particulate matter is demonstrated in the packing technique found necessary for the shipping to P.E. and the air filtration necessary to eliminate the spots problem associated with overcoating. Particulate filter analyses have not been extensive enough to identify levels and kinds of particular contaminants. Preliminary indications are that the particle sizes to be removed may be in the .1 to 10 micron range. Additional work in this area will be required.

The actions taken to correct the known laboratory air problems are listed below:

- 1) "Sealed" room
- 2) Barnebey Cheney air purification units
- 3) Humidifier/Dehumidifier; 41% RH
- 4) Heater/Air conditioner; 70°F
- 5) Pseudo-clean room procedures

Particular success has been achieved with one small coating room that has experienced essentially no problems since the start of the last contract period when the room was sealed off except for the special entrance. Installed within the room is a Barnebey Cheney activated charcoal air purification unit, a humidifier and dehumidifier, which holds relative humidity at 41%, and a heater and air conditioner, which holds the room at 70°F. Pseudo-clean room procedures have been instituted which consists of a routine cleaning schedule and wearing by all personnel of clean room clothes: booties, hat, lab coat and when necessary gloves and a face mask.

Reference

1. C. Aaron and C. C. Barker, J. Chem. Soc. 1963, 2655.

FIGURE 1

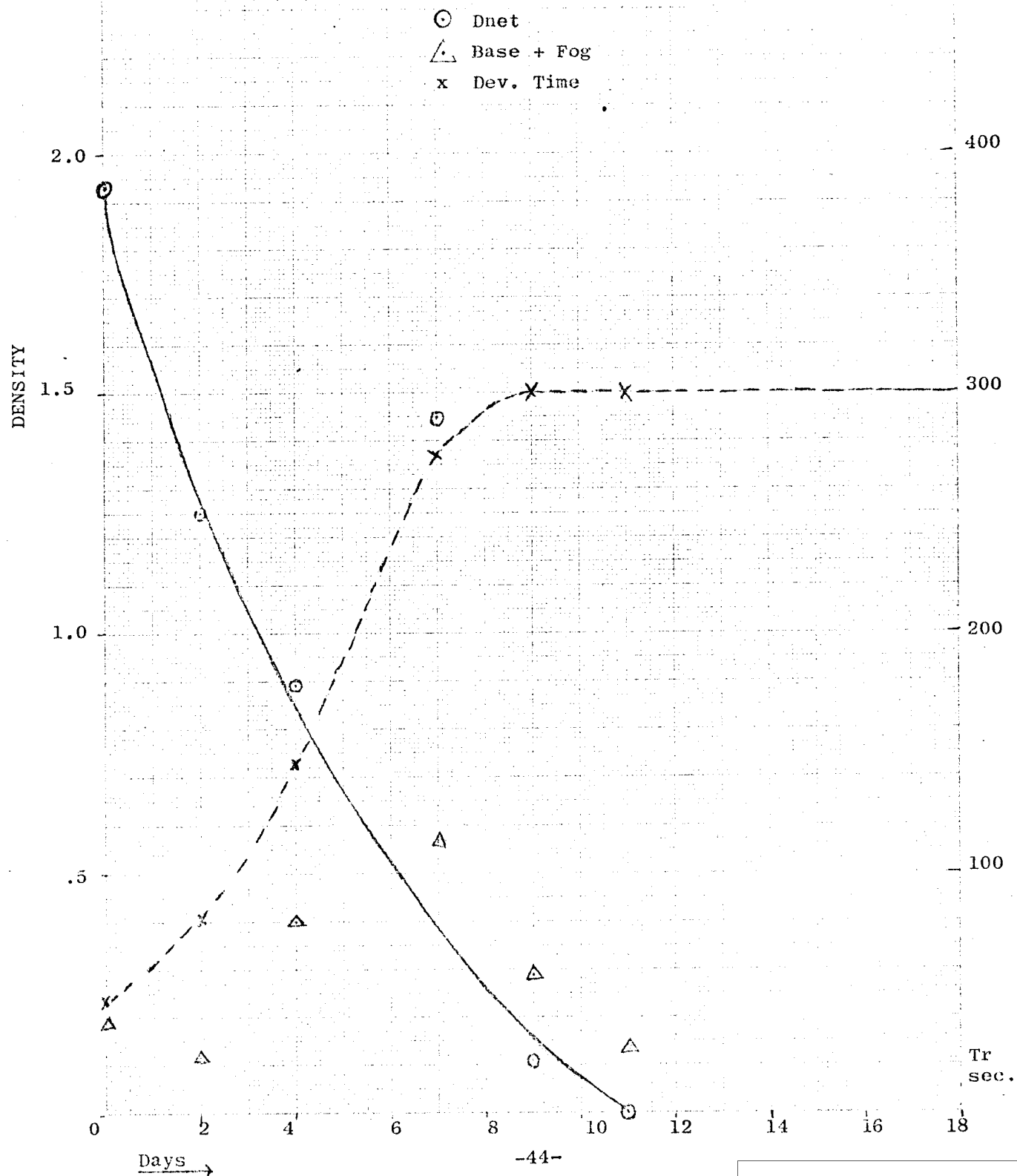
INGREDIENT INTERACTION DECAY STUDY
Solution 1D260 + D7 (No color reaction with benzene) +
Purified Benzene

FIGURE 2

INGREDIENT INTERACTION DECAY STUDY

SOLUTION II

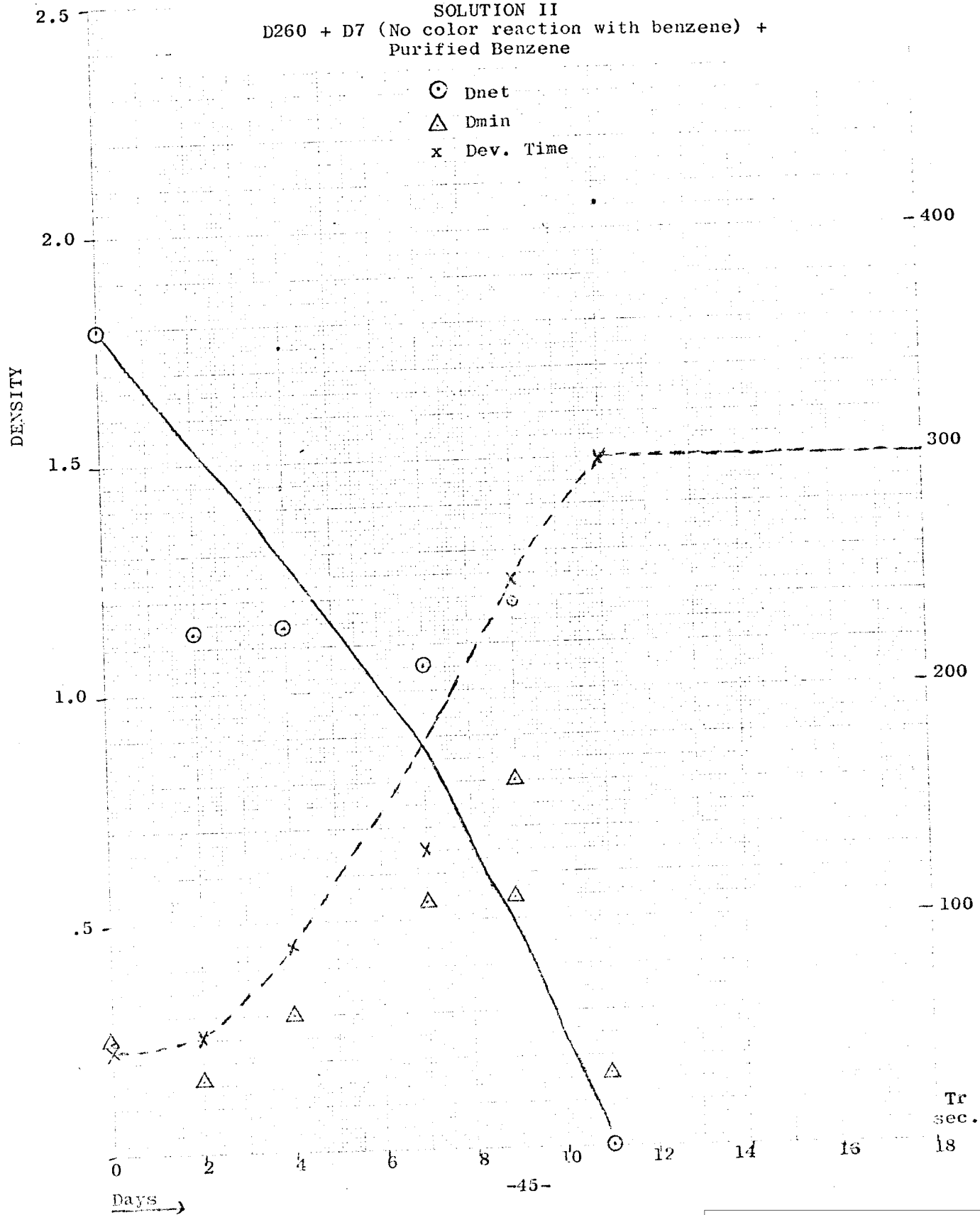
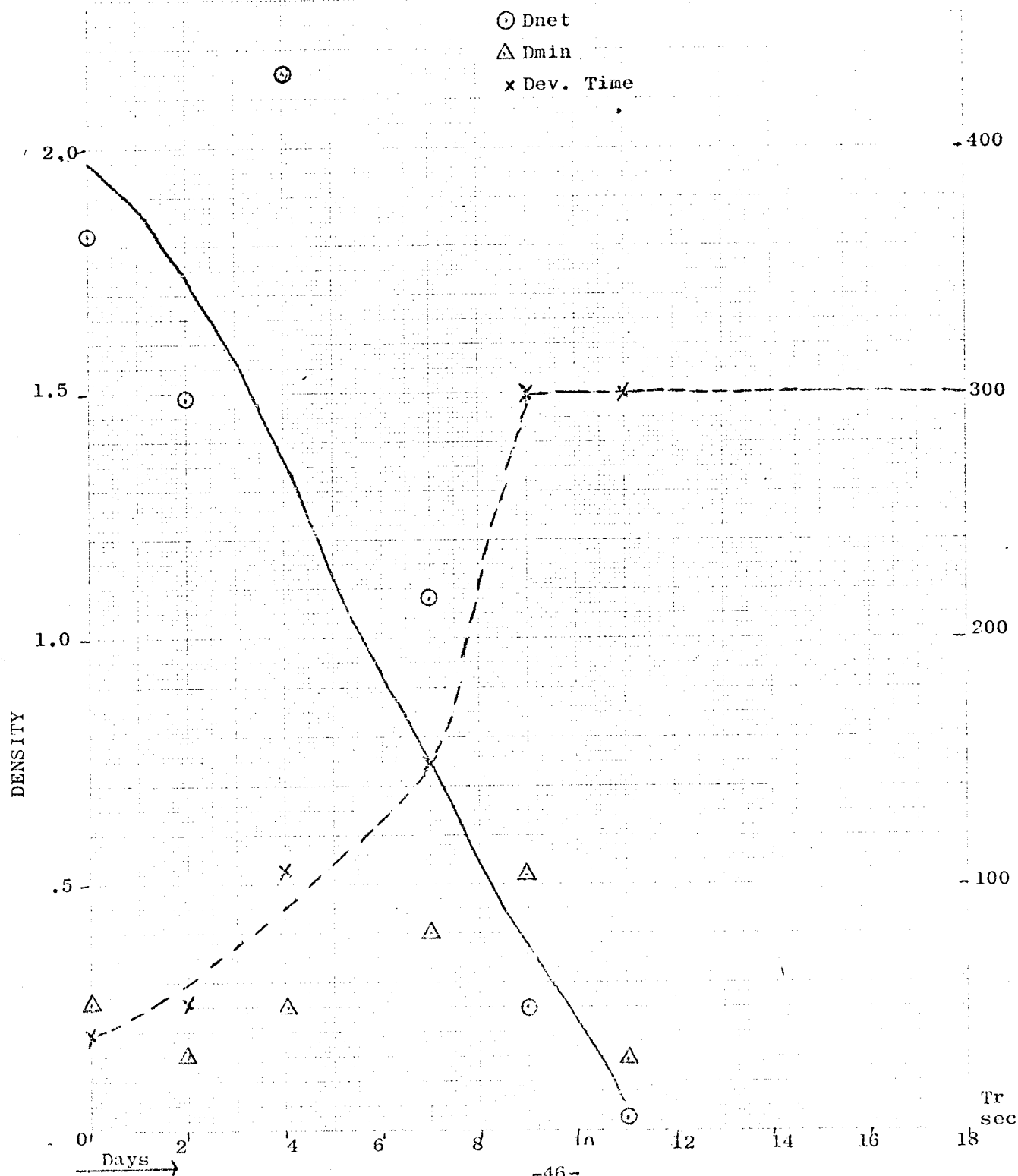
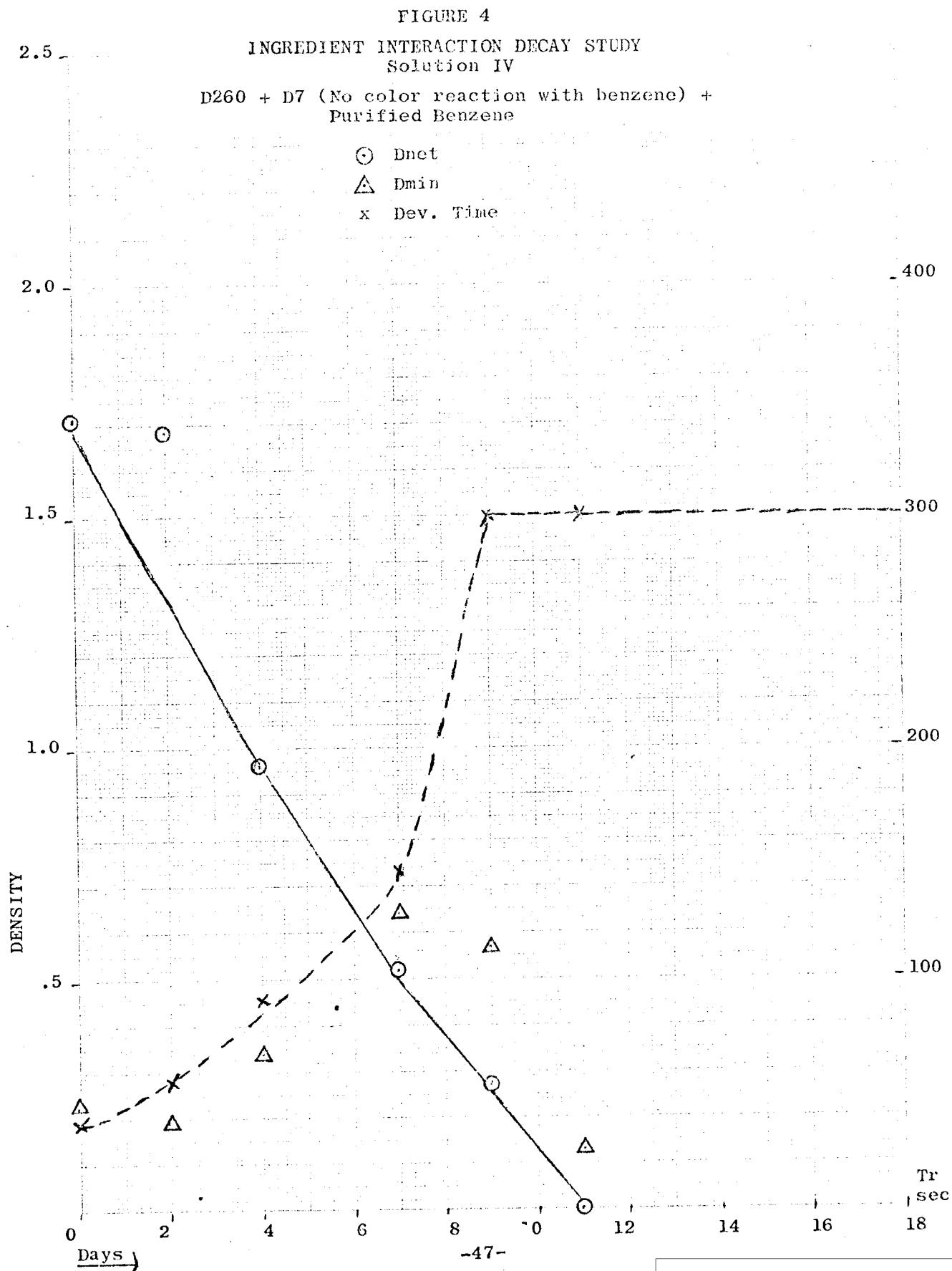
D260 + D7 (No color reaction with benzene) +
Purified Benzene

FIGURE 3

INGREDIENT INTERACTION DECAY STUDY
Solution IIID260 + D7 (No color reaction with benzene) +
Purified Benzene

-46-



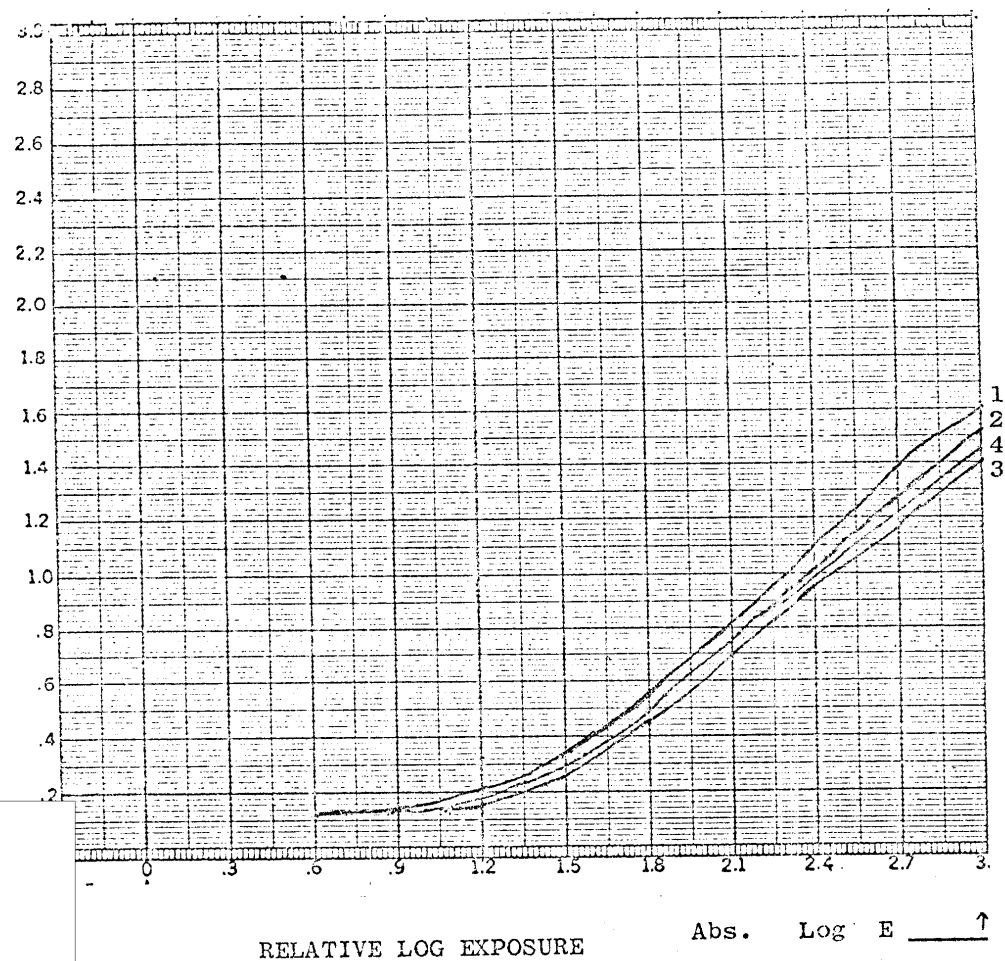


FIGURE 5
D263 Additions to Formula 5
(Printouts)

- 1) D263 100%
- 2) Formula 5 + 5% D263
- 3) Formula 5 + 1% D263
- 4) Formula 5 Control

25X1

25X1

25X1

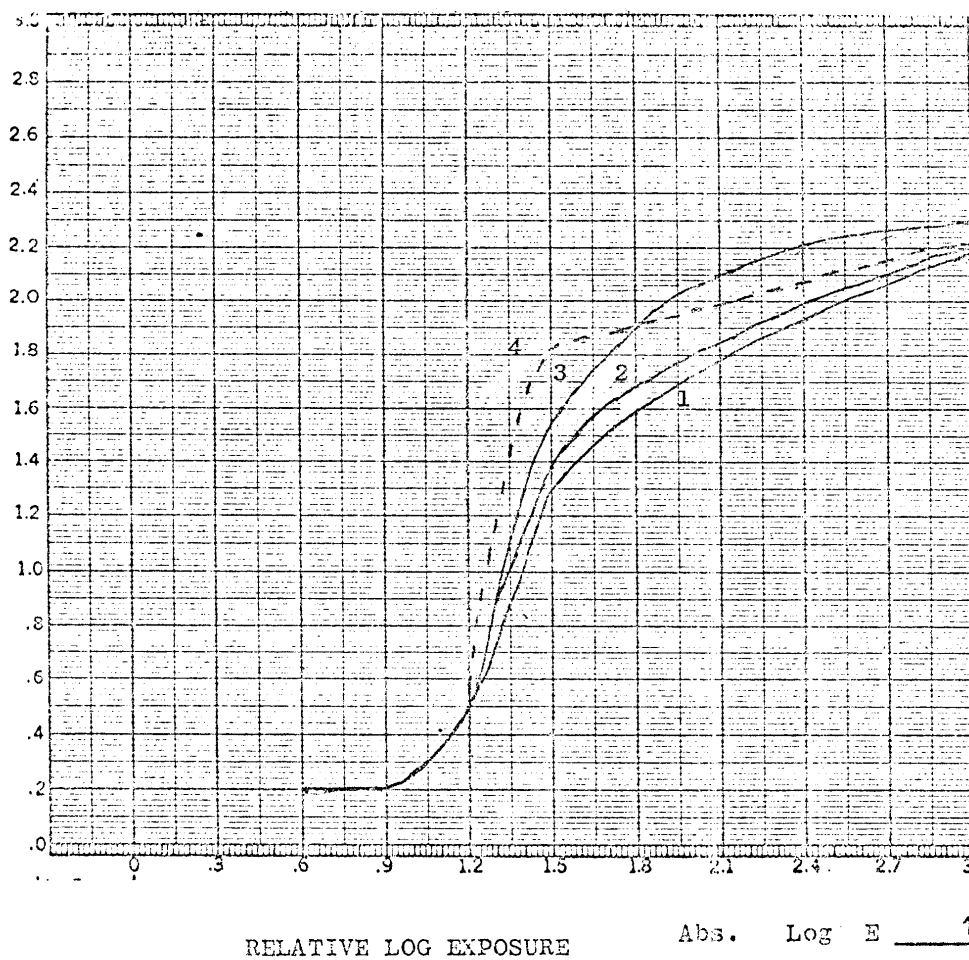


FIGURE 6

D263 Additions to 5/D7
(Optical Development)
 $T_e = .09$ sec.

- 1) 5/D7 Control; $T_r = 34$ sec.
- 2) 5/D7 + 1% D263; $T_r = 33$ sec.
- 3) 5/D7 + 5% D263; $T_r = 32$ sec.
- 4) D263 (100%); $T_r = 20$ sec.

25X1

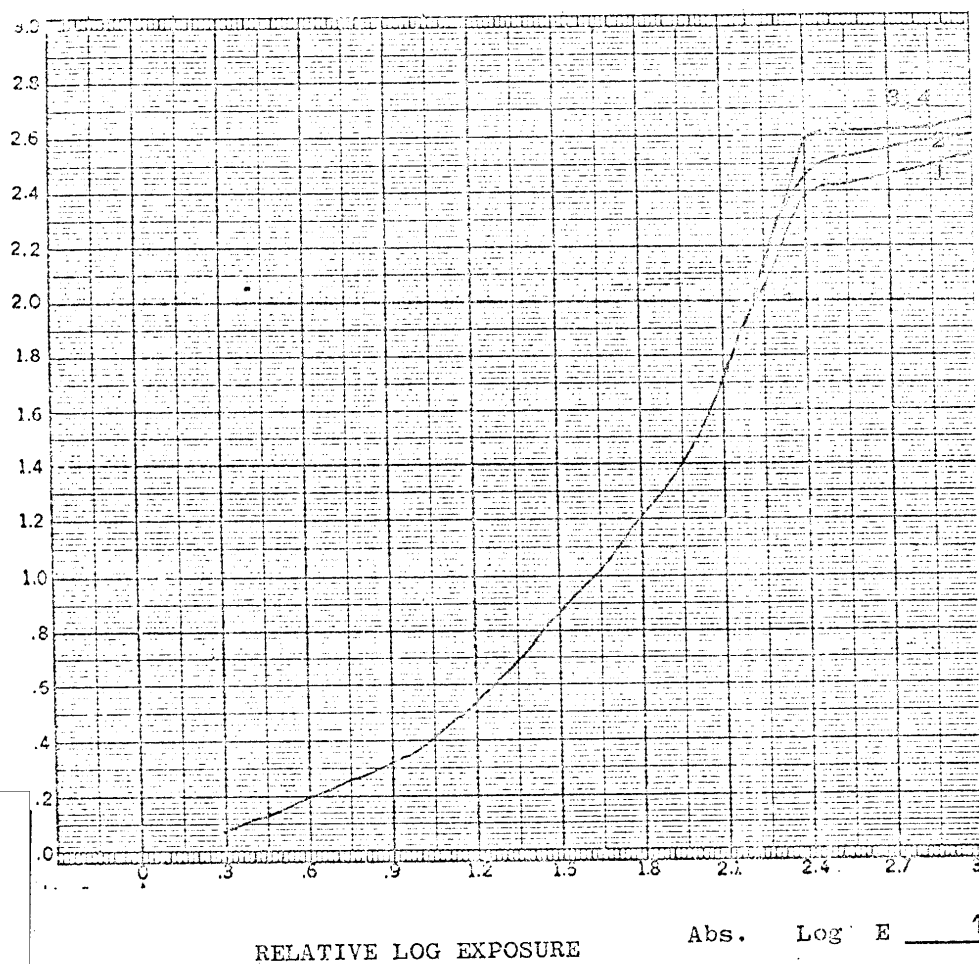


FIGURE 7
D263 Additions to 5/D7
(Printout)

- 1) 5/D7 Control
- 2) 5/D7 + 1% D263
- 3) 5/D7 + 5% D263
- 4) D263 (100%)

25X1

25X1

FIGURE 8

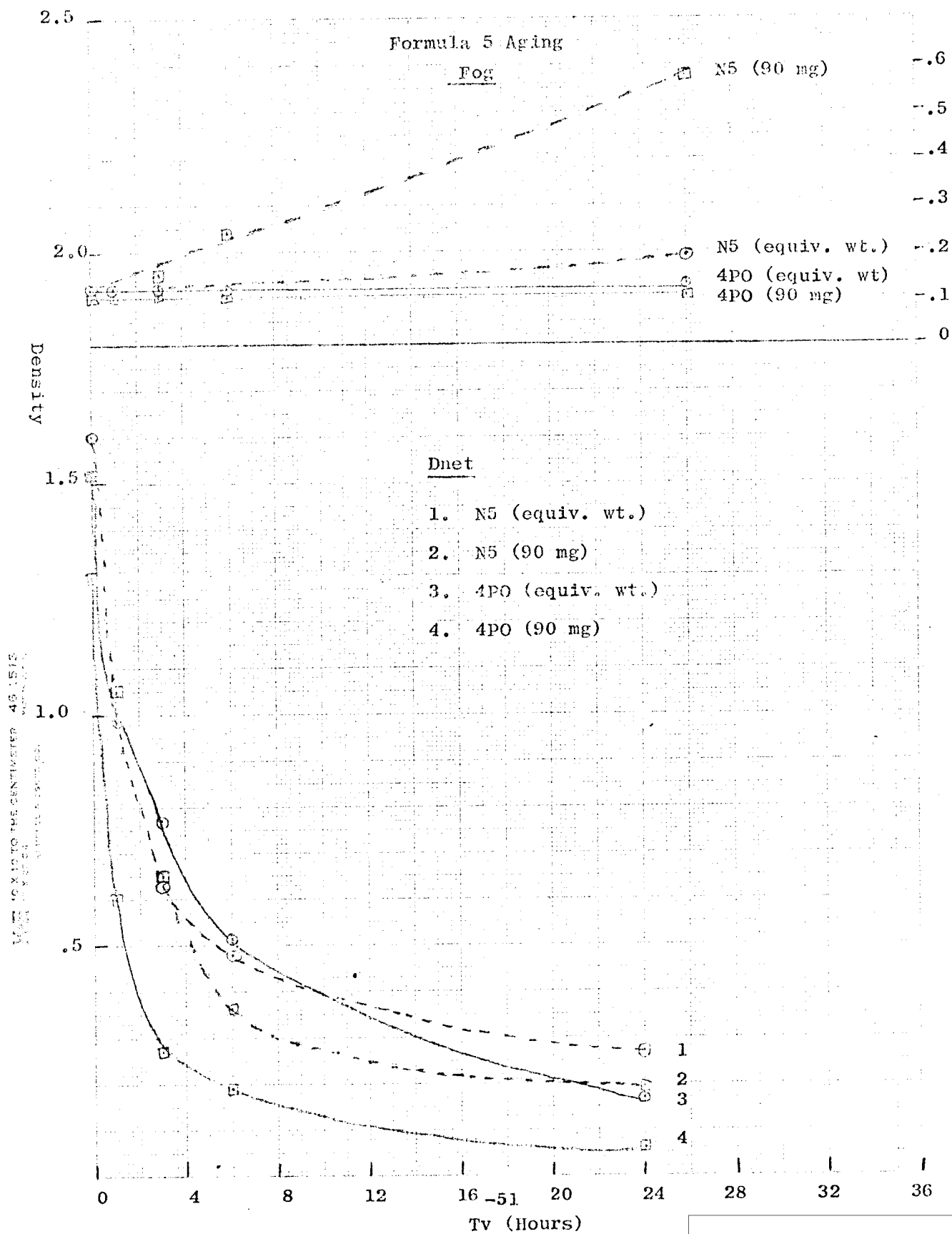


FIGURE 9

5/D7 Aging ($T_e=300$ sec.)

Dnet:

1. 4PO (equiv. wt.)
2. 4PO (90 mg)
3. N5 (equiv. wt.)
4. N5 (90 mg)
5. No PO

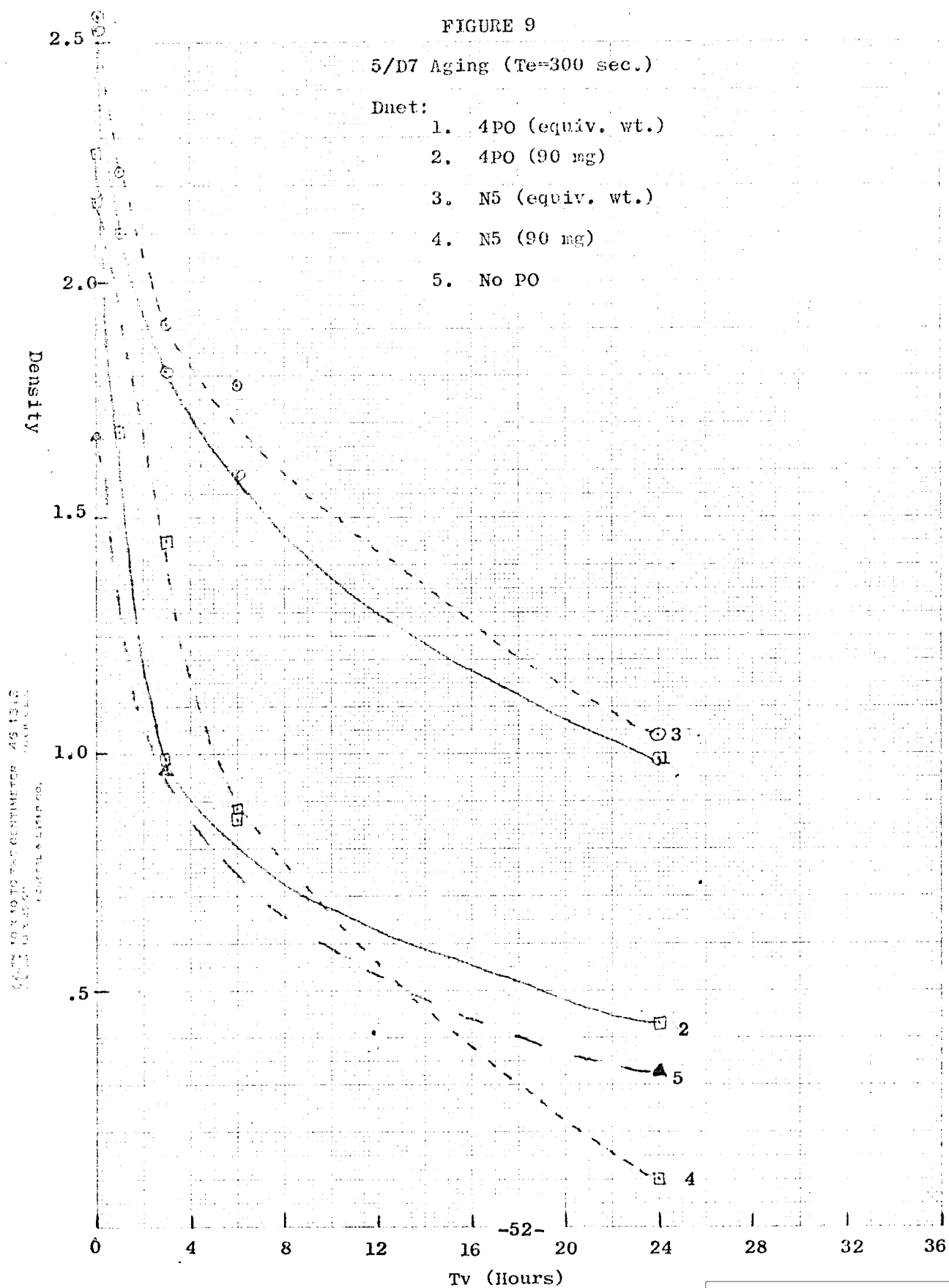
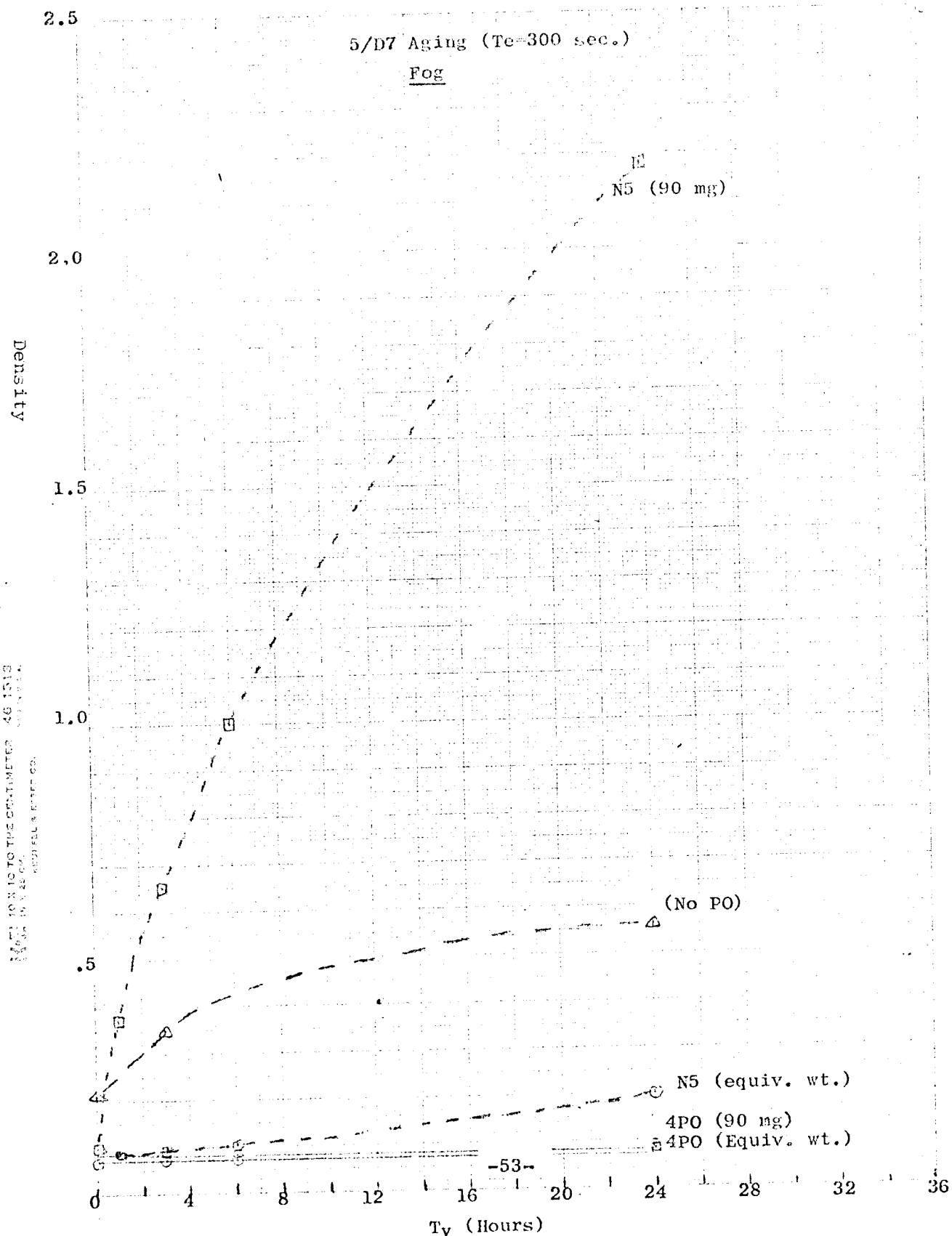


FIGURE 10



.07	.07	1.40	1.46	1.39	.50	.50	.66	.78	.92	1.08	1.20	A - G
.14	.20	1.20	1.30	1.36	.65	.76	.86	1.00	1.14	1.33	1.40	B - G
.18	1.26	1.40	1.55	1.61	1.64	.96	.96	1.08	1.19	1.30	1.46	C - G
.08	.08	1.05	1.03	.36	.42	.50	.68	.84	.96	1.14	1.29	D - G
1	2	3	4	5	6	7	8	9	10	11		

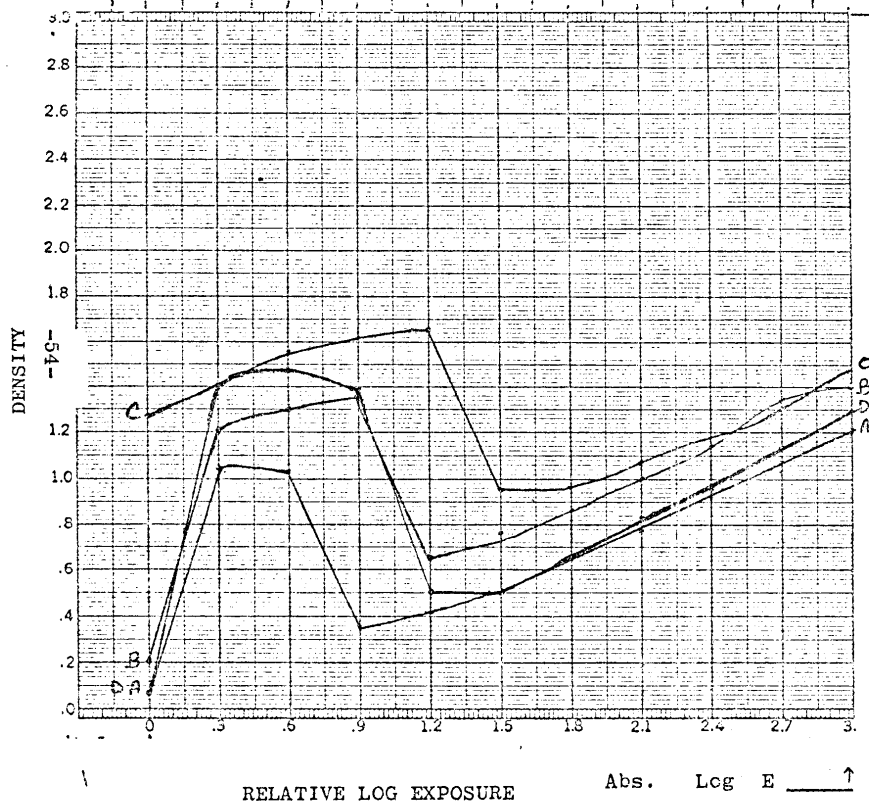


FIGURE 11
FORMULA 5/DPA
PRINTOUTS

- A - Original
Ref. 1825-31-14
- B - ØH Rex
Ref. 1825-25-8
- C - Anthranol Addition
Ref. 1825-31-3
- D - Plastanox + Distearyl TDP
Ref. 1825-31-29

25X1

25X1

25X1

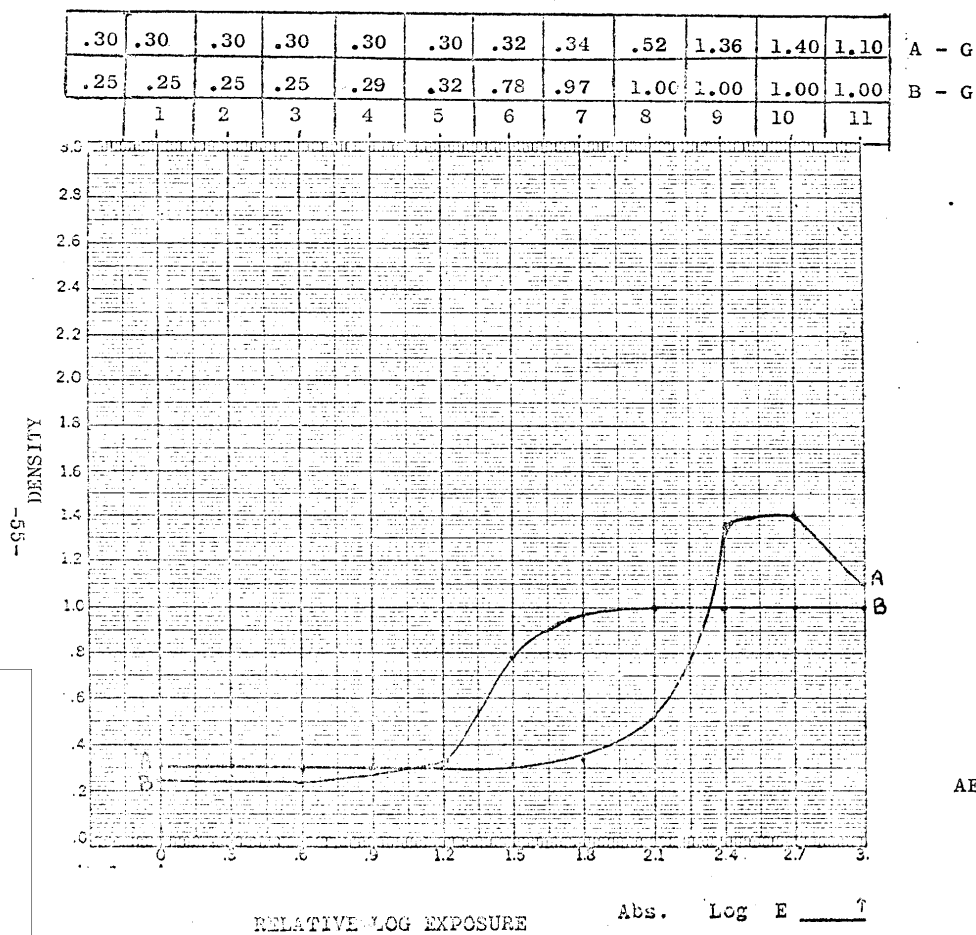


FIGURE 12
FORMULA 5/DPA

A - 15 minute Printout
Ref. 1825-21-17

B - 4 second Printout
Ref. 1825-21-16

γ A - 2.0
 B - 1.0

AEI A - .003
 B - .05

25X1

.06	.10	.14	.22	.32	.56	.90	1.30	1.86	2.32	2.46	2.60	A - B
.08	.12	.15	.23	.36	.59	.89	1.30	1.81	2.18	2.44	2.58	B - B
.08	.14	.19	.26	.41	.65	.96	1.33	1.80	2.25	2.39	2.53	C - B
1	2	3	4	5	6	7	8	9	10	11		

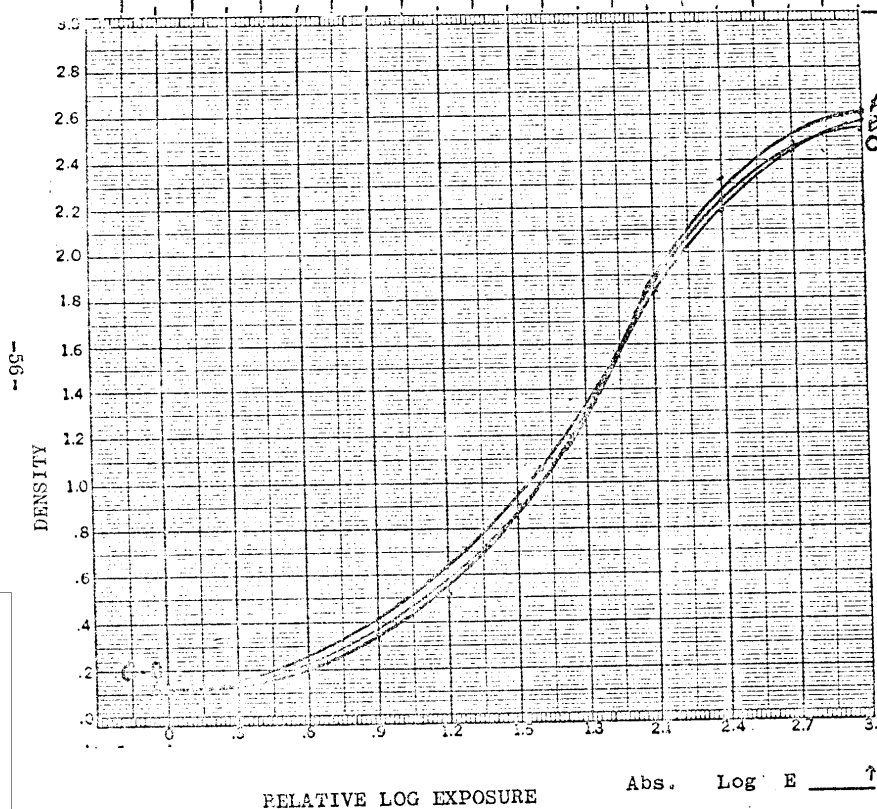


FIGURE 13
FORMULA 5/D7
PRINTOUTS

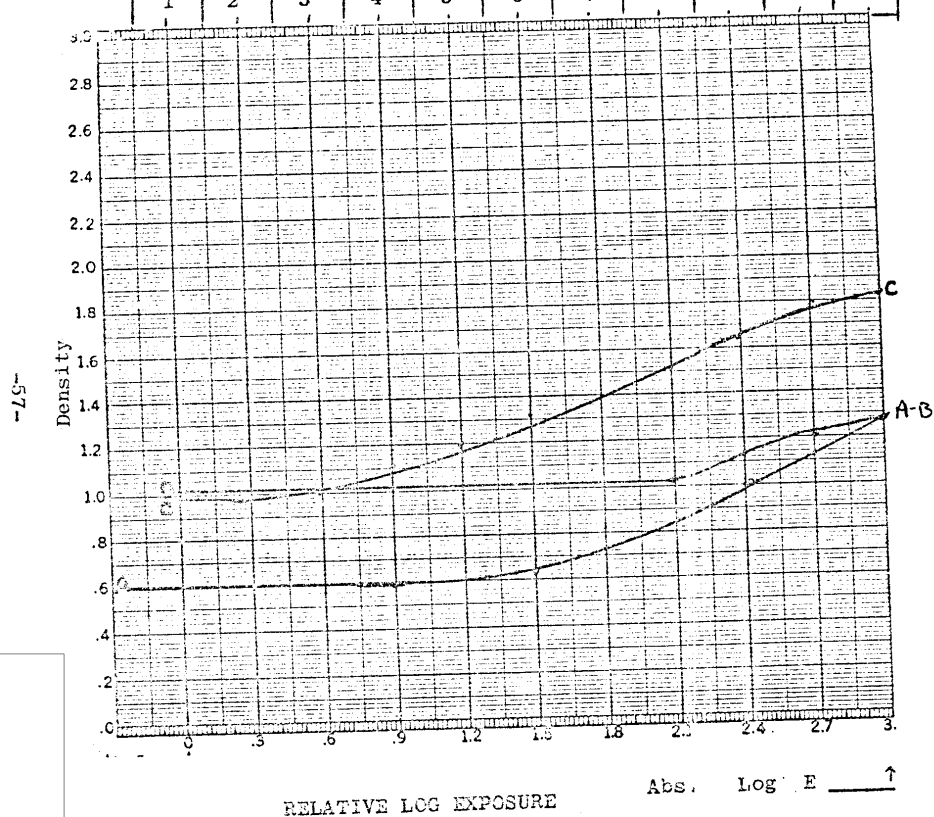
- A - Control
Ref. 1824-31-14
- B - 22.5 mg Dilauryl TDP
Ref. 1875-11-11
- C - 5.6 mg Distearyl TDP
Ref. 1875-11-12

25X1

25X1

25X1

.58	.58	.58	.58	.58	.61	.65	.73	.85	1.00	1.12	1.28	A - G
1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.12	1.20	1.28	B - G
.98	.98	.98	1.00	1.10	1.20	1.32	1.40	1.51	1.64	1.78	1.82	C - G
1	2	3	4	5	6	7	8	9	10	11		



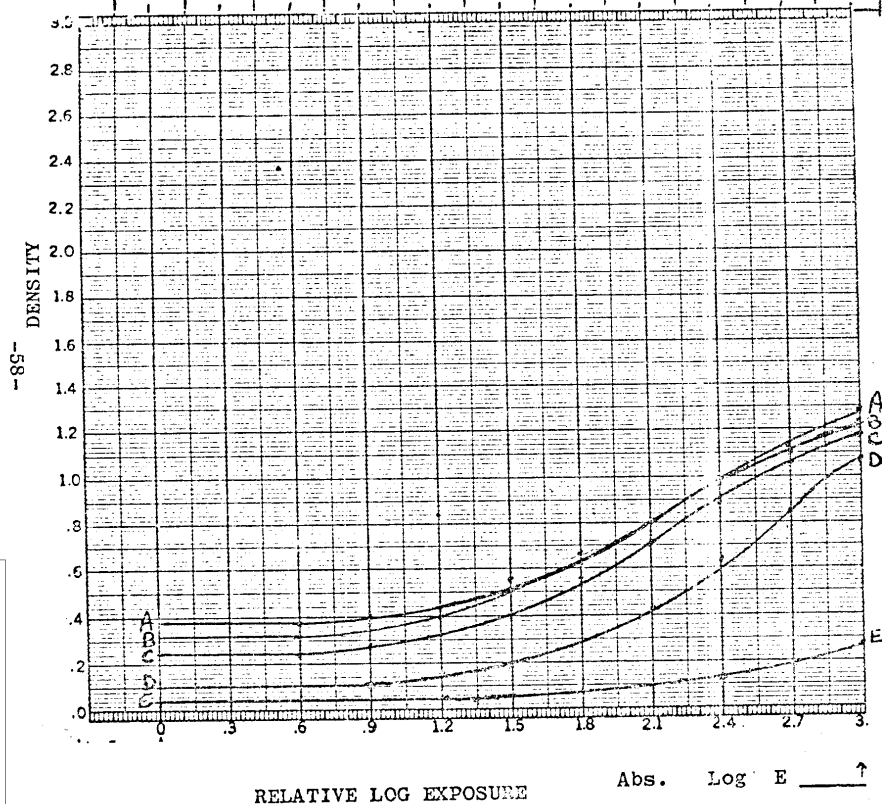
25X1

25X1

.37	.37	.37	.37	.40	.43	.55	.68	.80	.97	1.12	1.28	A - G
.32	.32	.32	.32	.38	.40	.50	.62	.80	.96	1.10	1.24	B - G
.24	.24	.24	.24	.28	.32	.40	.56	.70	.88	1.06	1.18	C - G
.10	.10	.10	.10	.10	.16	.18	.26	.42	.64	.84	1.06	D - G
.04	.04	.04	.04	.04	.04	.05	.07	.09	.12	.18	.26	E - G
1	2	3	4	5	6	7	8	9	10	11		

FIGURE 15
FORMULA 5/DPA
PRINTOUTS

- A - Control
Ref. 1825-31-14
- B - 2.25 μ g Michlers Hydrol
Ref. 1825-31-16
- C - 22.5 μ g Michlers Hydrol
Ref. 1825-31-17
- D - 67.5 μ g Michlers Hydrol
Ref. 1825-31-18
- E - 1 mg Michlers Hydrol
Ref. 1825-31-15



25X1

25X1

.10	.10	.10	.10	.14	.19	.30	.46	.66	.86	1.03	1.16	C - G
.37	.37	.37	.37	.40	.43	.55	.68	.80	.97	1.12	1.28	A - G
.11	.11	.13	.24	.30	.32	.40	.54	.66	.82	.96	1.16	B - G
.04	.04	.04	.04	.04	.04	.06	.10	.26	.48	.76	1.00	D - G
1	2	3	4	5	6	7	8	9	10	11		

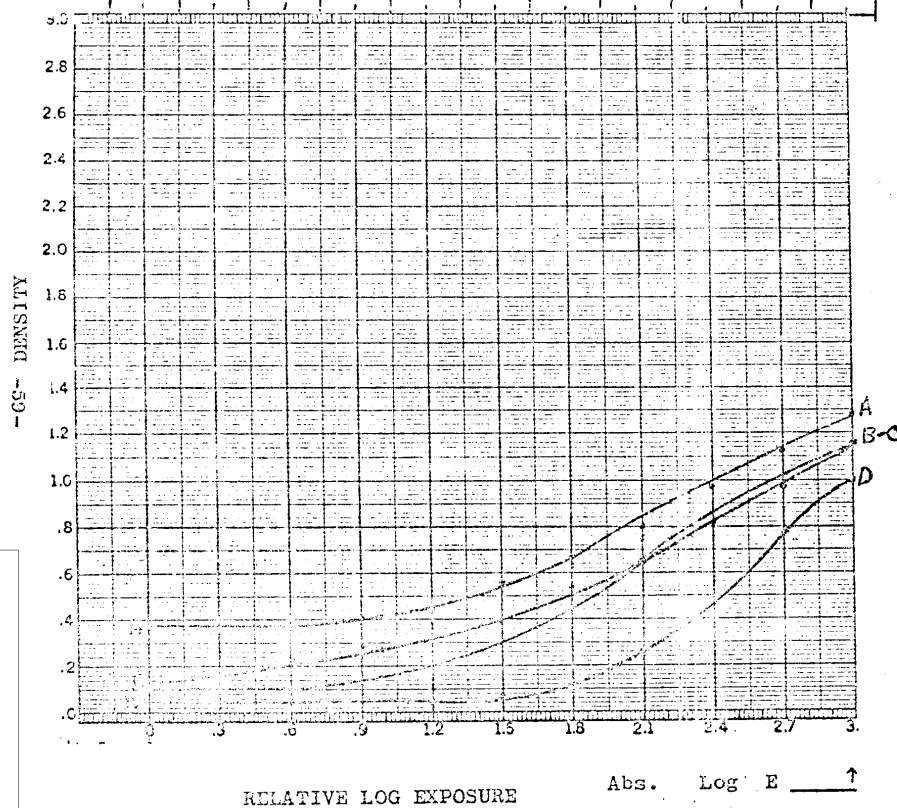
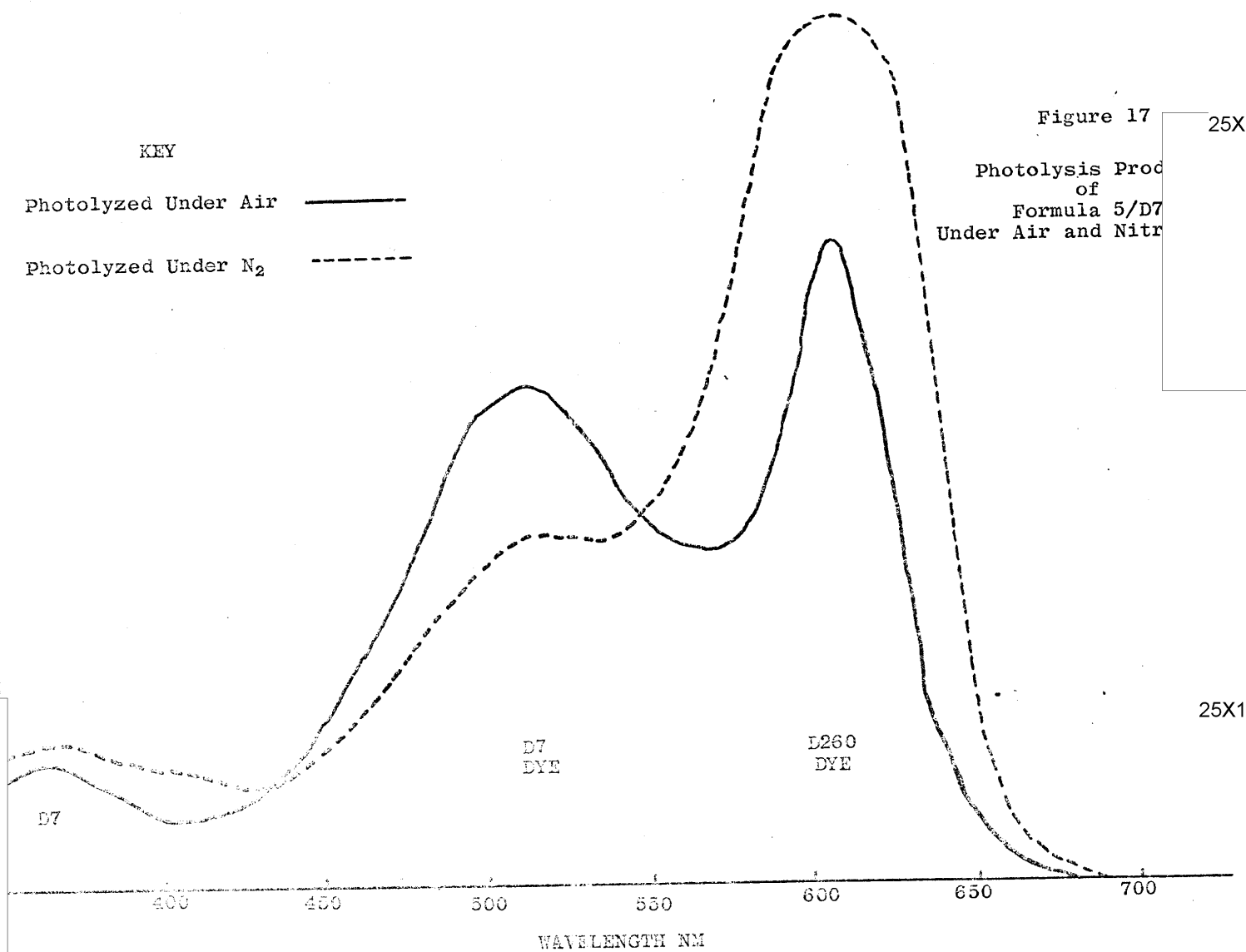


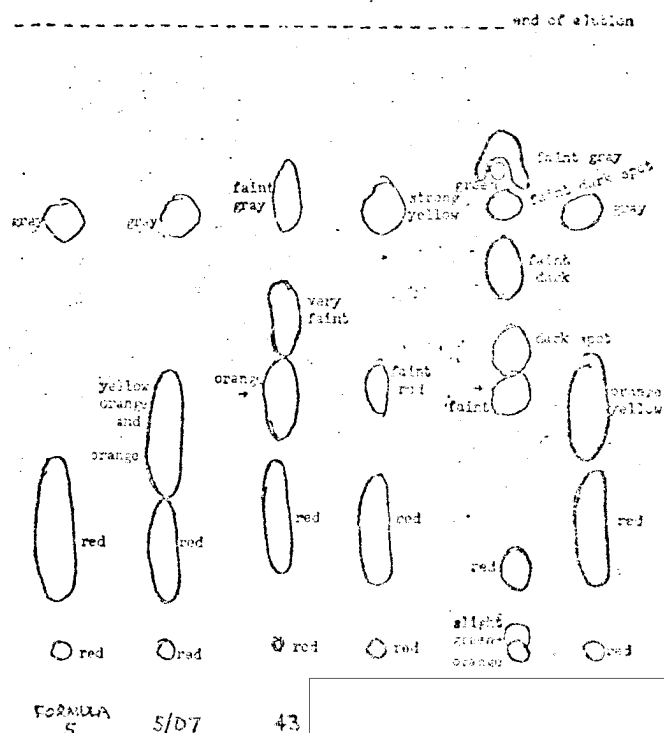
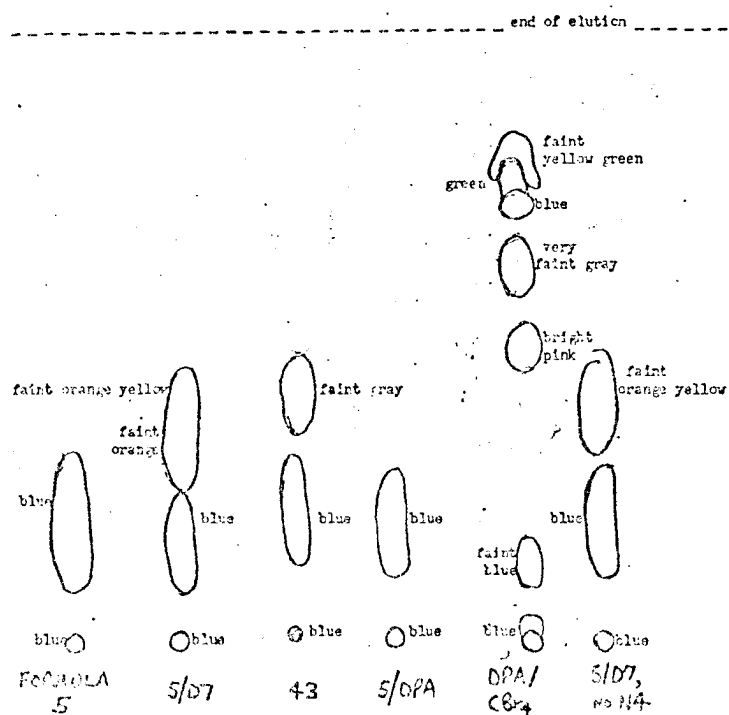
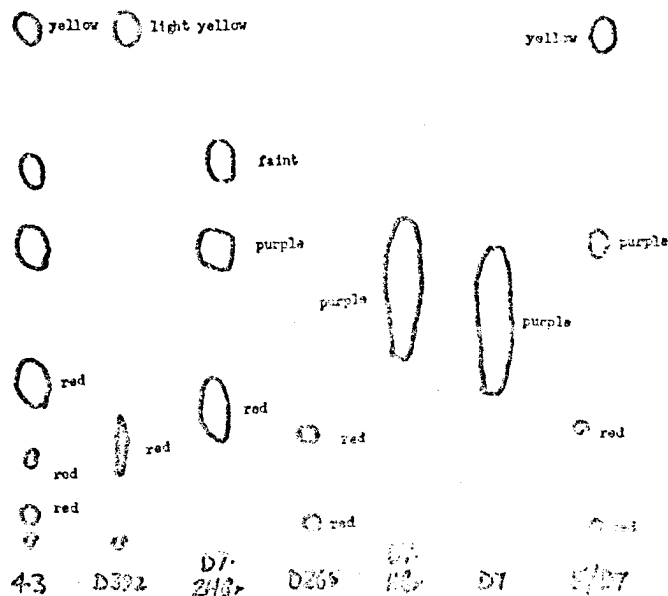
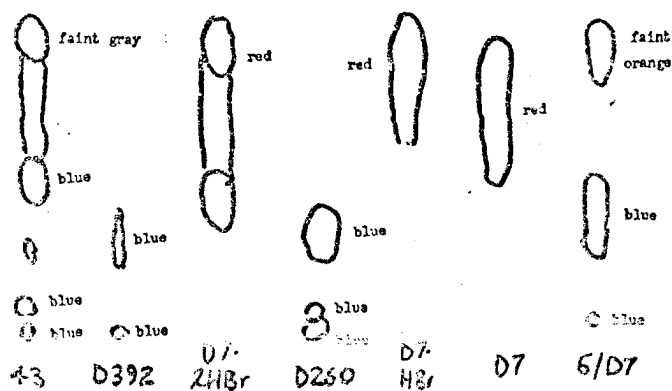
FIGURE 16
FORMULA 5/DPA
PRINTOUTS

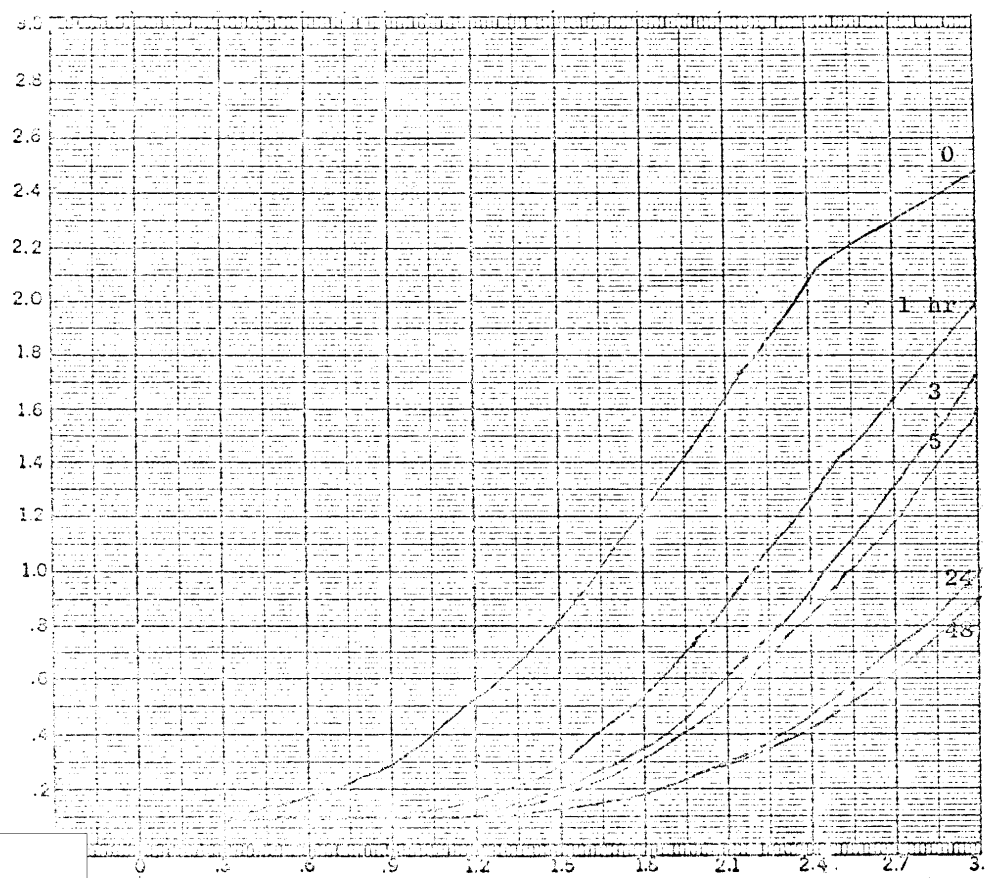
- A - Control
Ref. 1825-31-14
- B - 100 µg Plastanox 425
Ref. 1825-31-22
- C - 225 µg Plastanox 425
Ref. 1825-31-21
- D - 1 mg Plastanox 425
Ref. 1825-31-19

25X1



Dye Separation on Analytical Silica Plates





RELATIVE LOG EXPOSURE

Abs. Log E \uparrow

FIGURE 19

1867-44

5/D7 Control
Aging

Te = 300 sec.
Printout

25X1

25X1

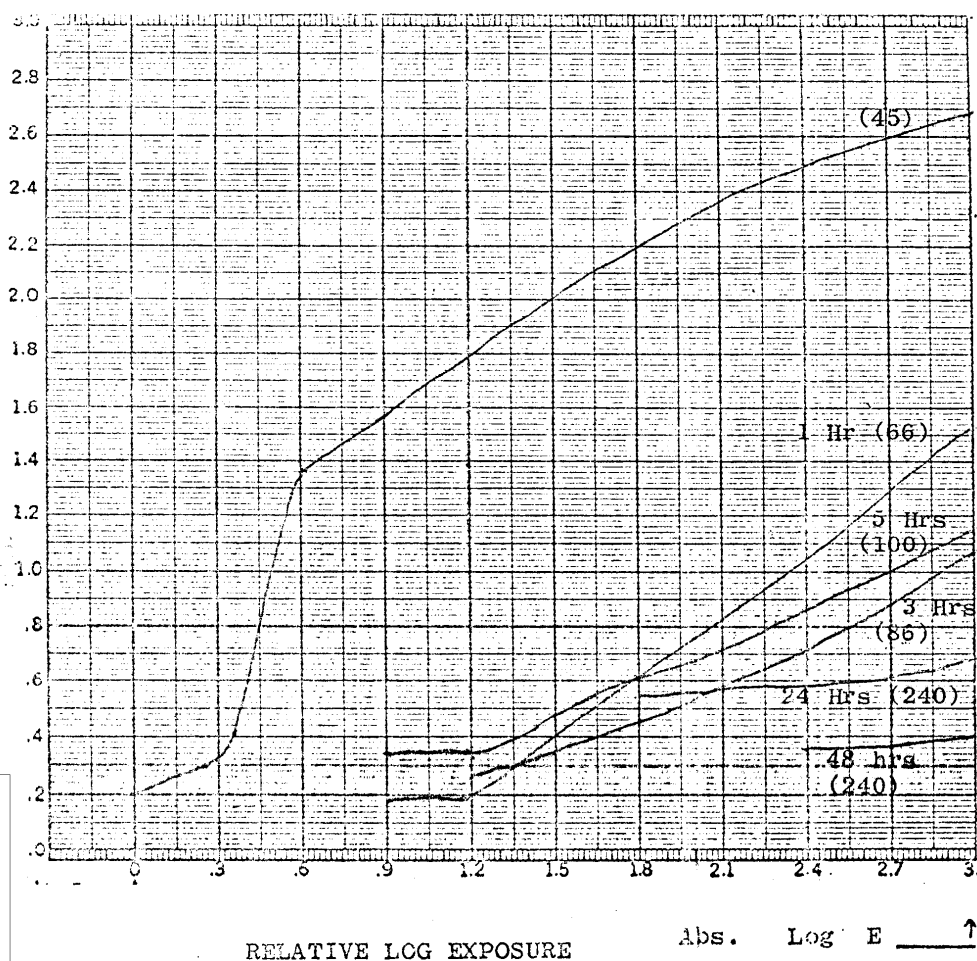


FIGURE 20

1867-44

5/D7 Control
Aging

Te = 5 sec.

Optical Development
(Tr = sec.)

25X1

25X1

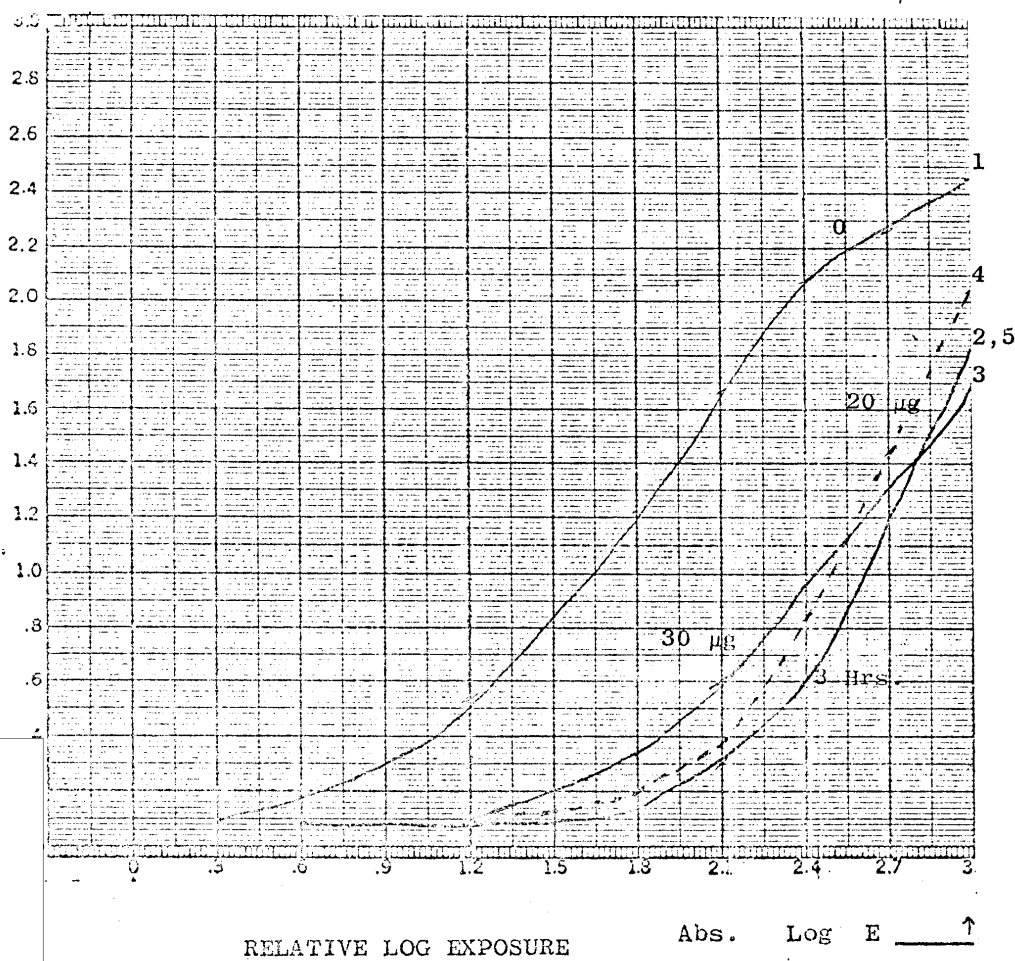


FIGURE 21

5/D7
Printouts
5/D7 Control + 4DMAP

25X1

25X1

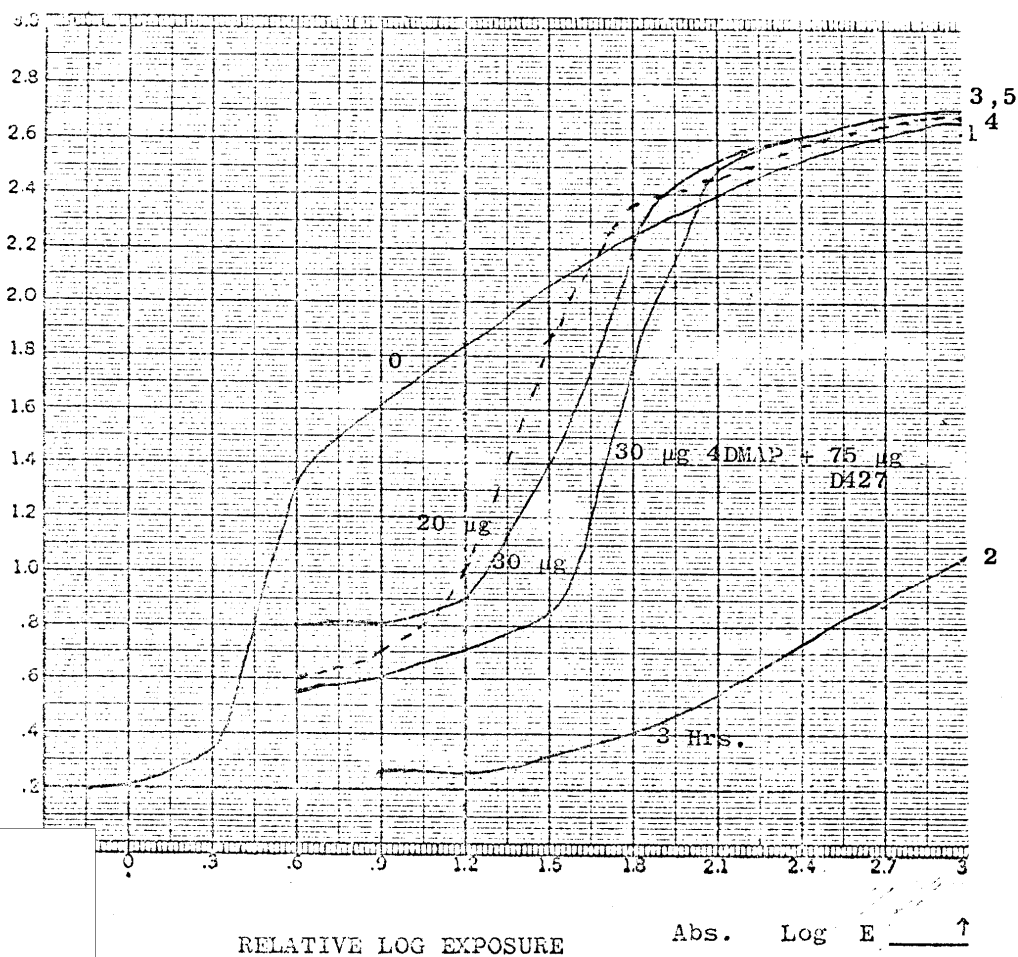


FIGURE 22
5/D7
+
4DMAP
Optical Development

- 1) Tv = 0; Tr = 45 sec
- 2) Tv = 3 hrs.; Tr = 8 sec
- 3) Tv = 0; Tr = 660 sec.;
30 µg 4DMAP
- 4) Tv = 0; Tr = 570 sec.;
20 µg 4DMAP
- 5) Tv = 0; Tr = 720 sec.;
30 µg 4DMAP; + 75 µg D427

25X1

25X1

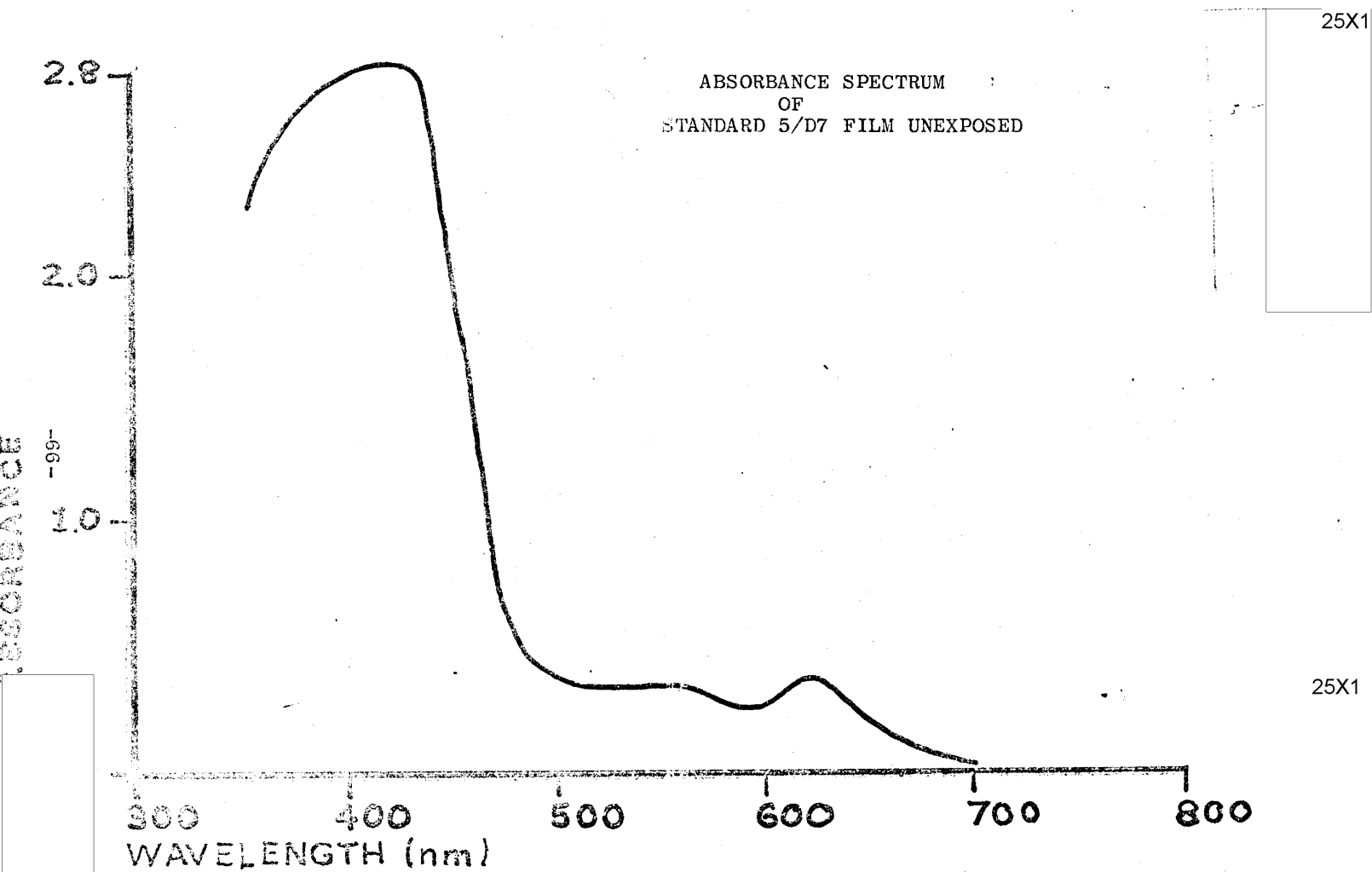
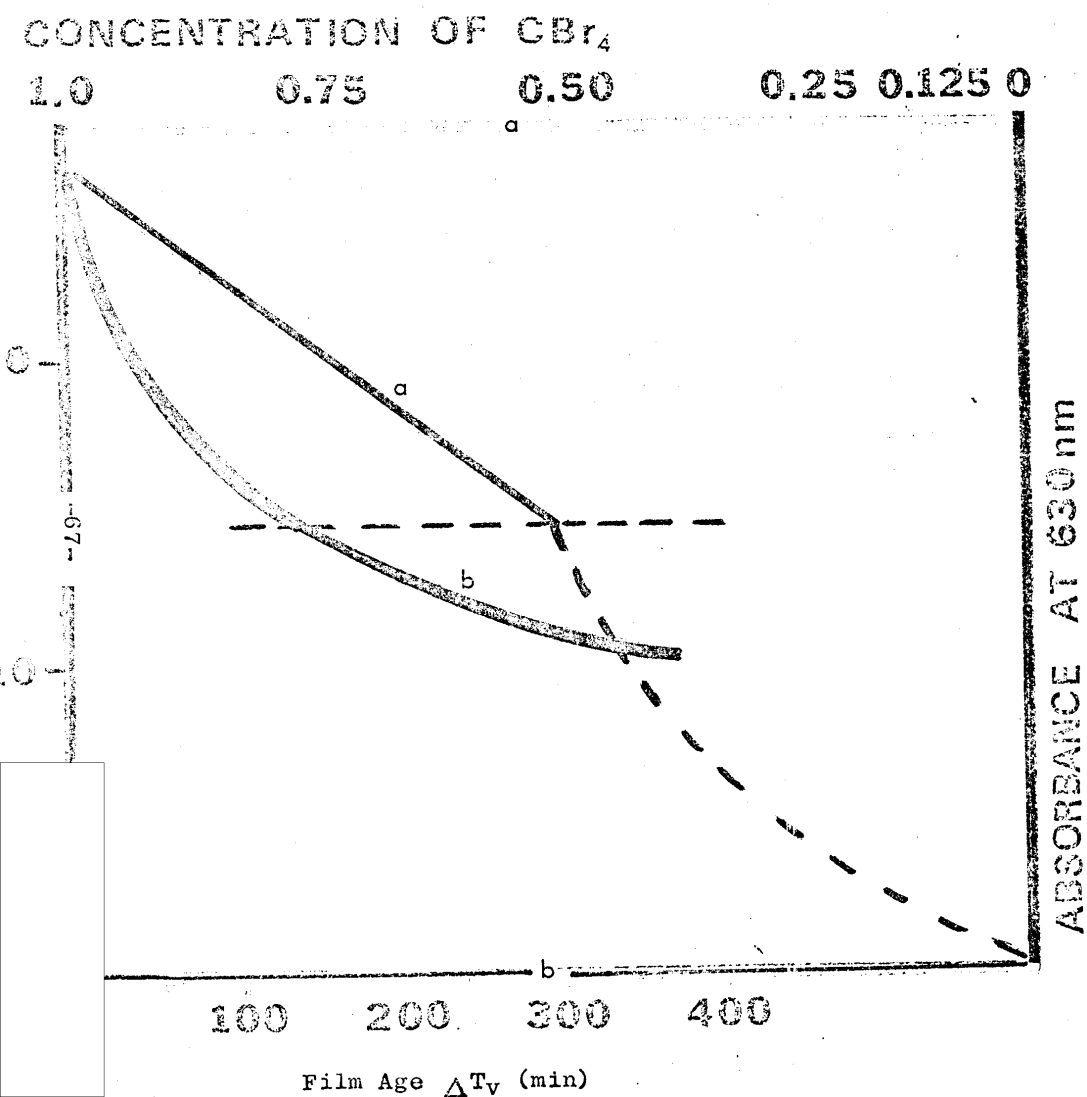


FIGURE 23



Loss of Activator
 CBr_4

25X1

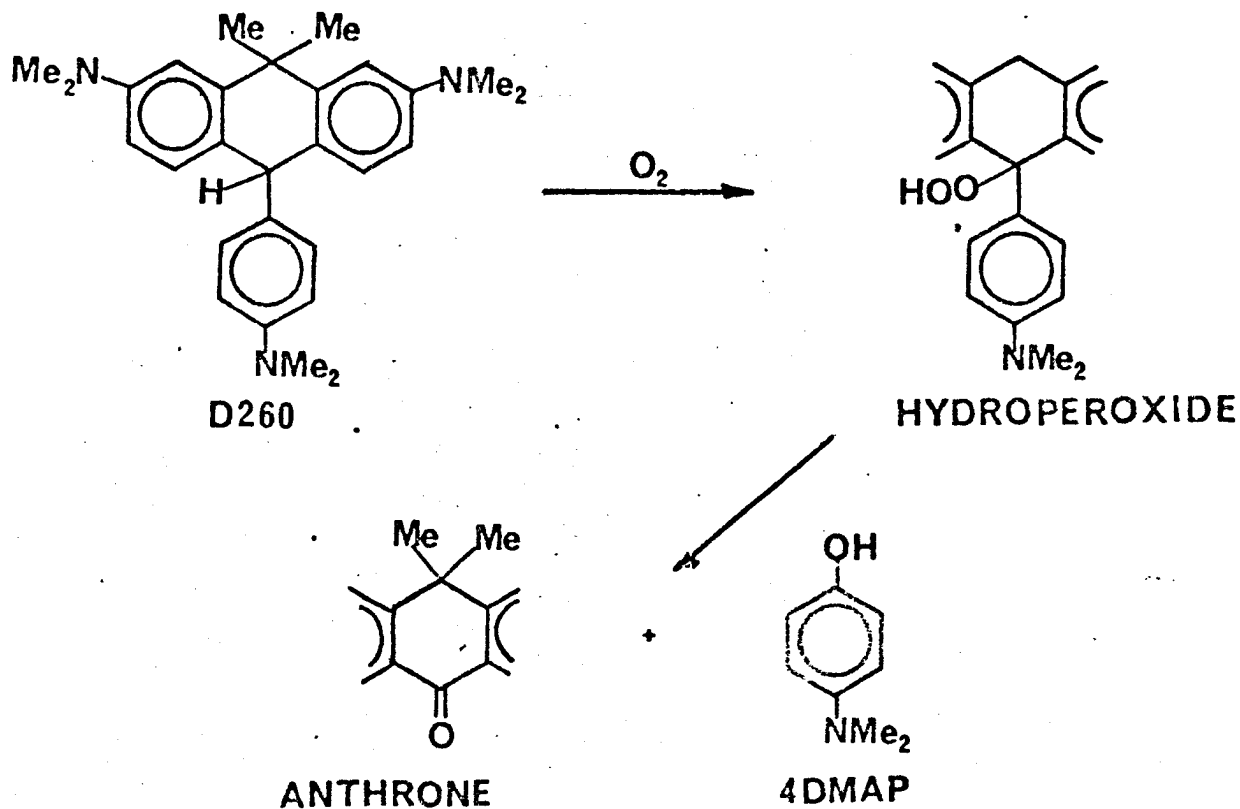
a Concentration
of CBr_4 As Fraction
of Standard Formula

b Aging
of Standard Film

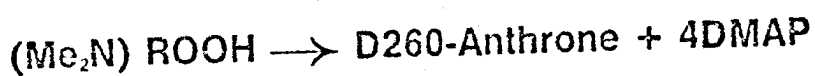
25X1

FIGURE 24

ANISM OF CHEMICAL SPEED DECAY



or



Autoxidation Chain

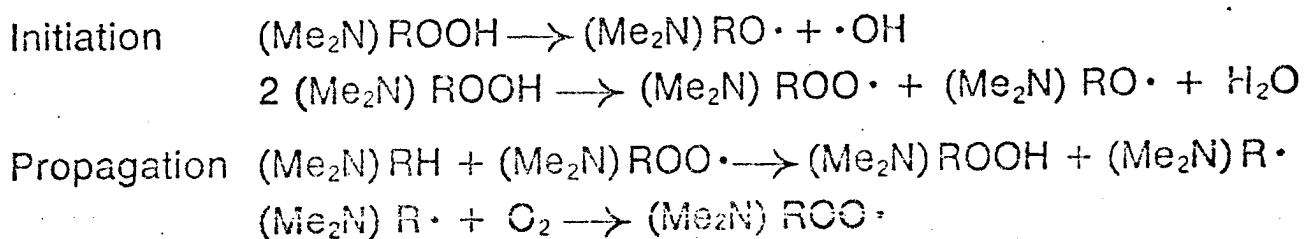


FIGURE 26

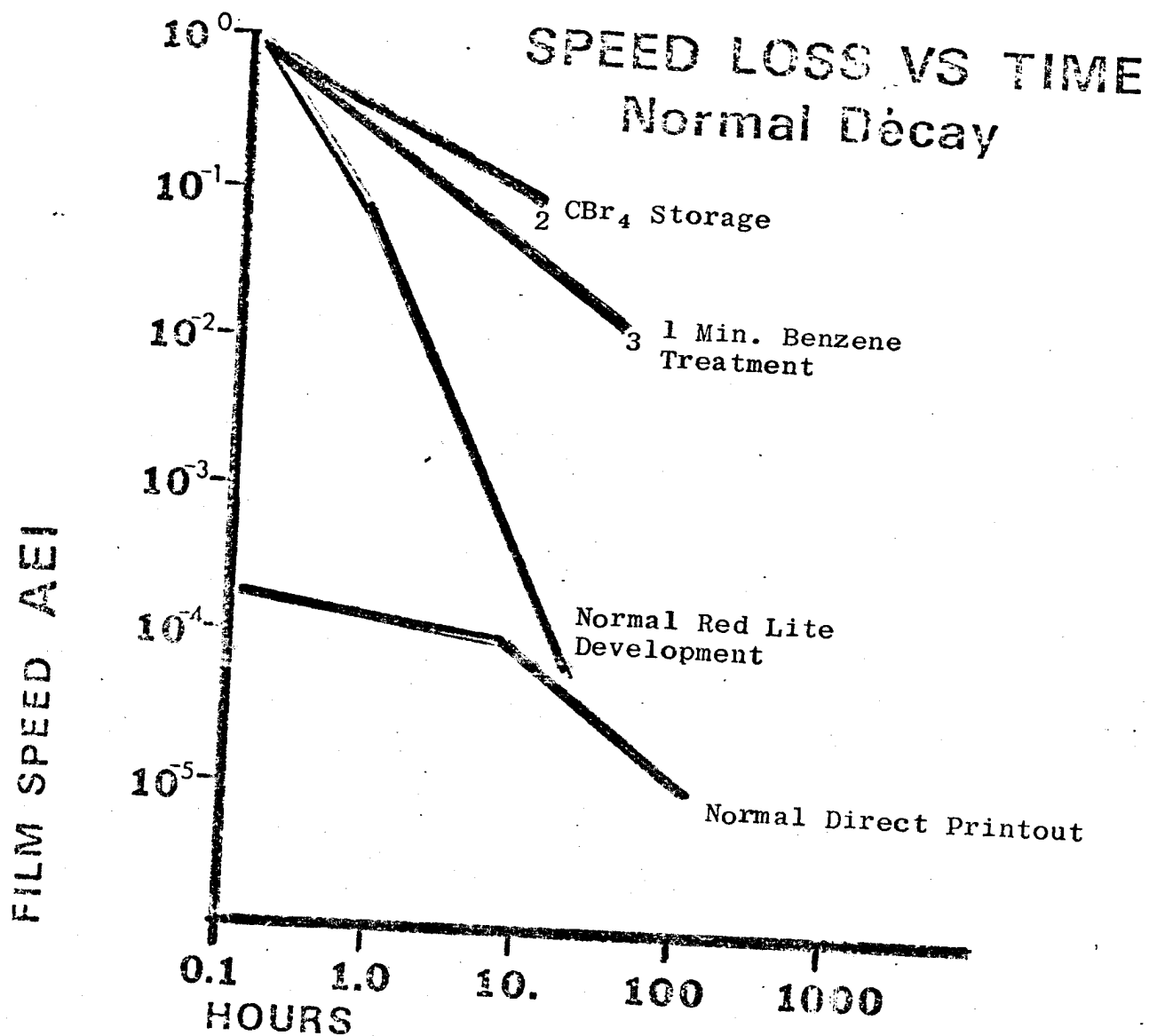
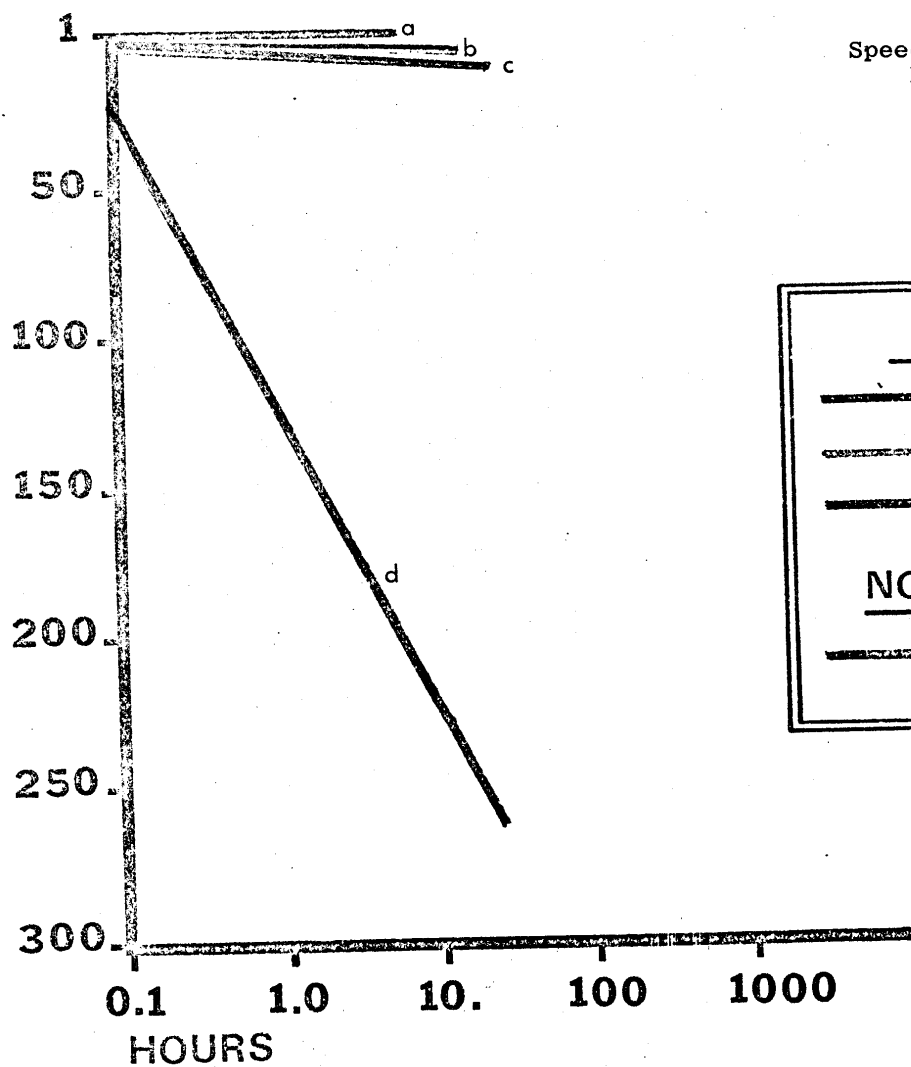


FIGURE 27

Speed Loss Factor vs. Time
Direct Printout



OVERCOATED

a 5 Min.

b 30 Min.

c 60 Min.

NOT OVERCOATED

d Control

25X1

25X1

SPEED LOSS VS TIME Overcoated RLD Samples

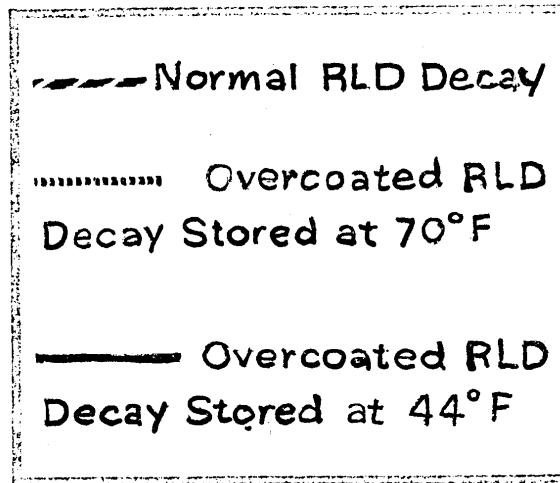
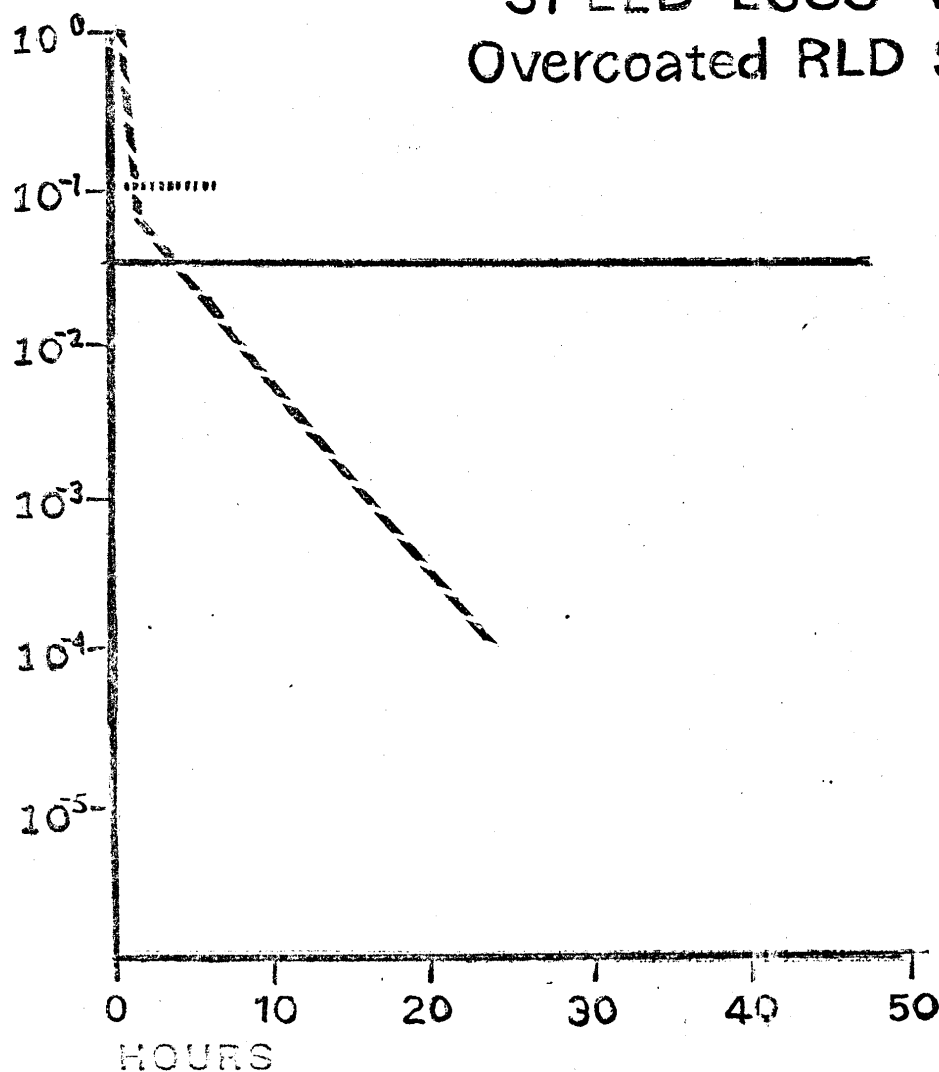


FIGURE 28

CHARACTERISTIC CURVES Overcoated Samples

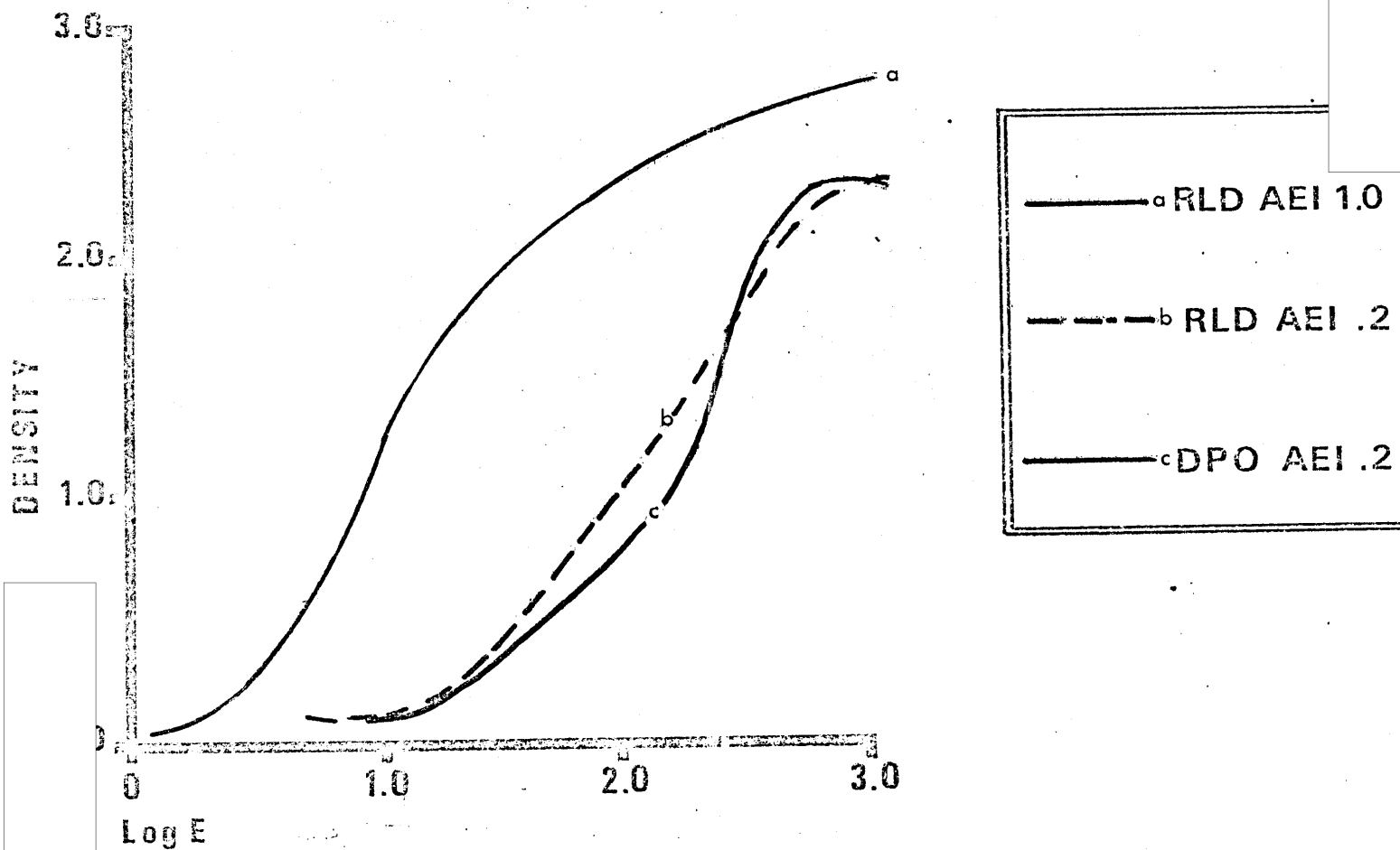


FIGURE 29

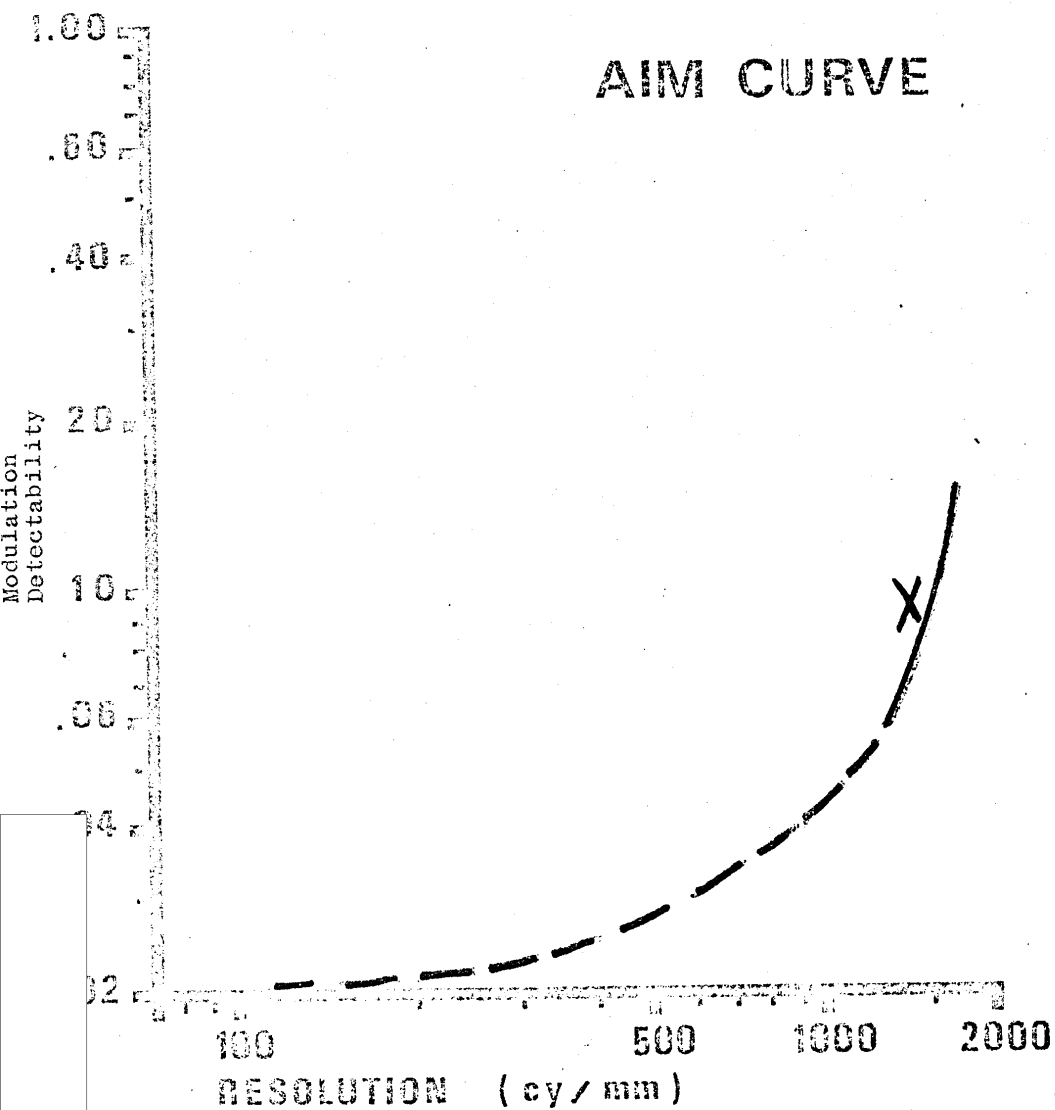


FIGURE 30

Prev
RLD Aim Curve
X Overcoated
RLD sample Points

25X1

25X1

FIGURE 31

Project 325B - Interface
Shipment 8 - Coated April 17, 1972
Formula 5/D7
See Table 7 for data

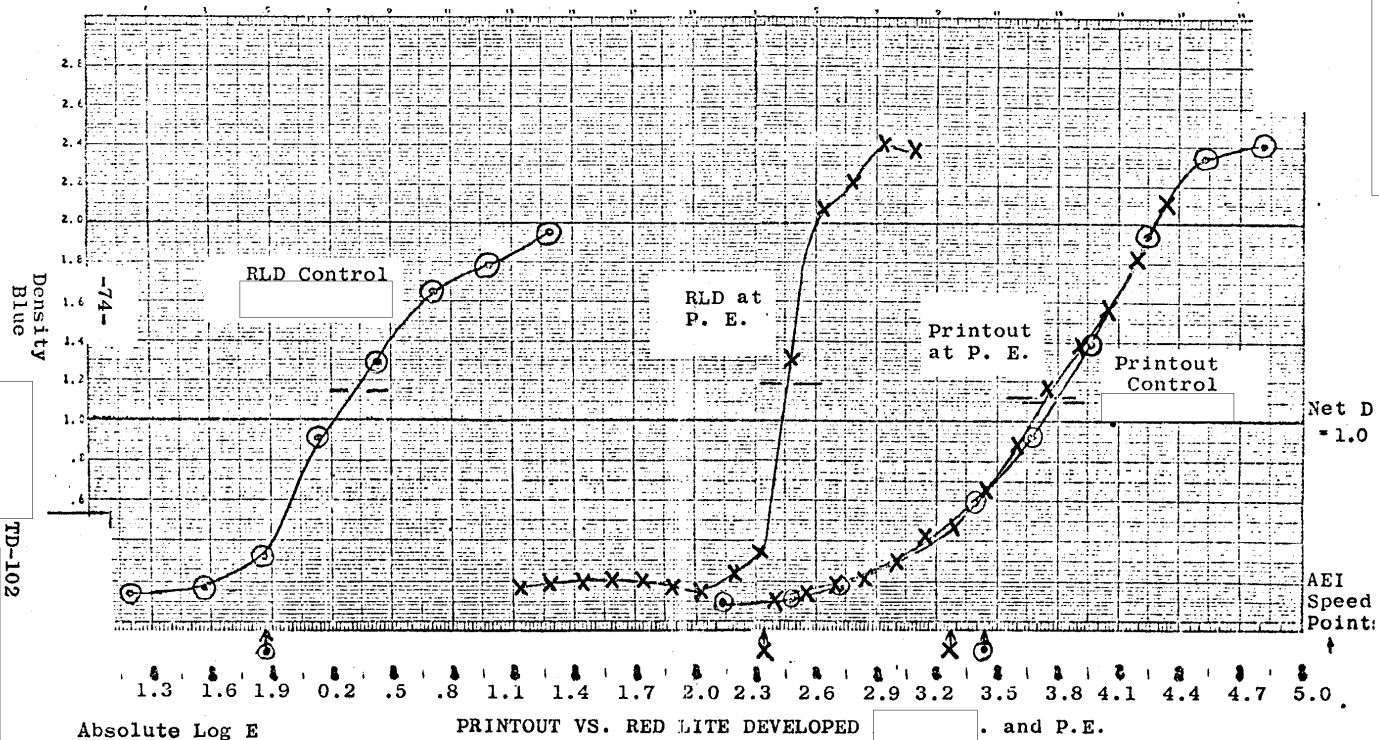
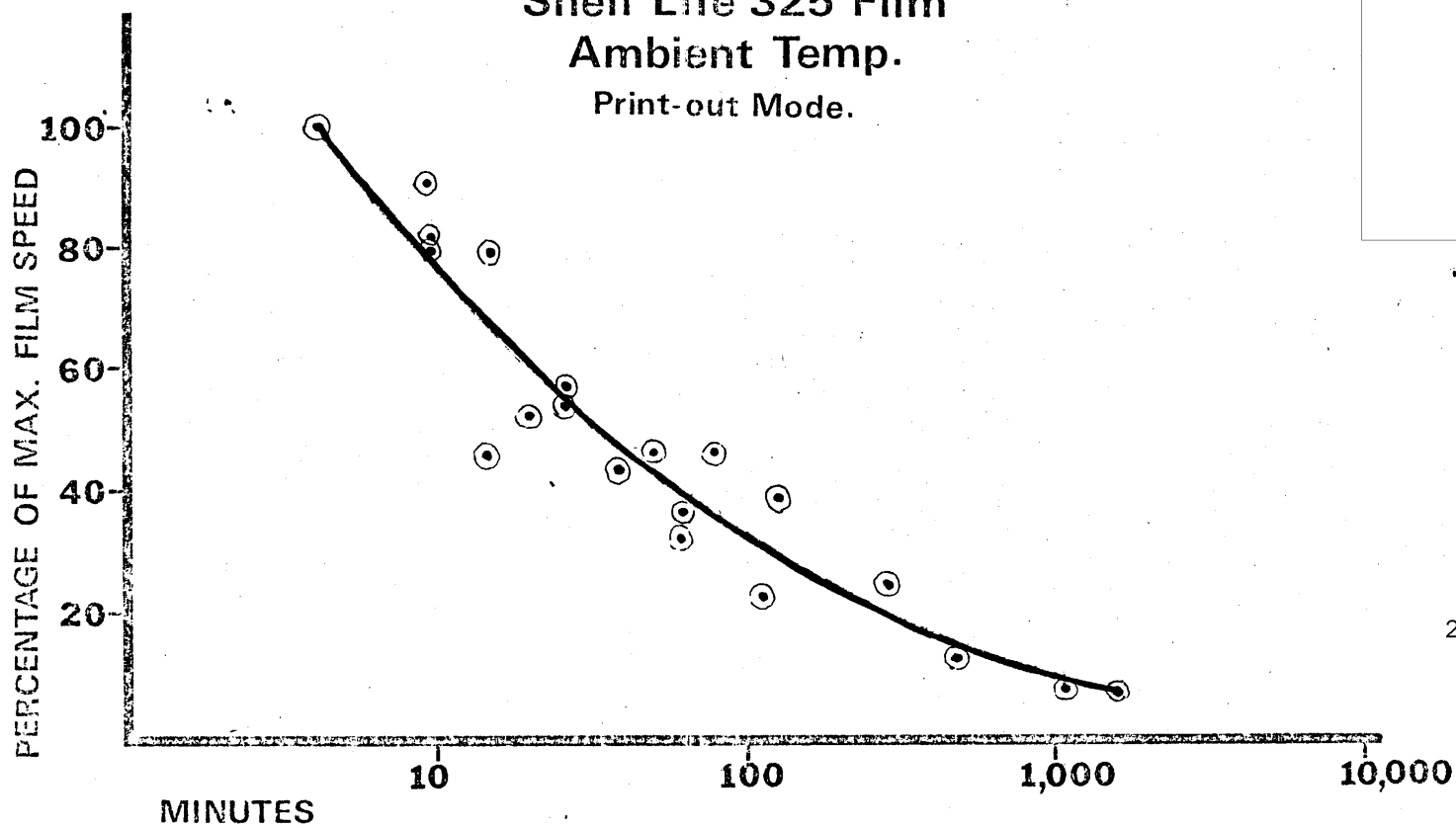


FIGURE 32

INTERFACE
Shelf Life 325 Film
Ambient Temp.
Print-out Mode.



25X1

25X1

100 mg D260
64 mg D7
2.25 ml 10% P.S. Sol.
2.25 ml Chr. Sol.
Corresponding N-Oxide

TABLE 1
N-Oxide Study
Formula 5/D7

Exp. No.	P	AEI	Dmax B	Dmin B	Dnet B	Dmax G	Dmin G	Dnet G	Δ Tr (sec.)	N-Oxide	Comments
<u>Heteroaromatic N-Oxides</u>											
Control 5	1.7	.52	1.61	.23	1.38	1.68	.21	1.47	140	N4	Control Film 1756-26-1 through 18
20	-	-	.89	.49	.40	.90	.59	.31	360	N1	Fog and Image Very Red
17	-	-	1.26	.88	.48	1.19	.81	.38	300	N2	Faint Image, Heavy Red Fog
5A	-	-	.87	.45	.42	.95	.46	.49	260	N3	Faint Image, Heavy Red Fog
1	-	-	1.40	1.29	.11	1.23	1.15	.08	300	None	Little Image Under Red Fog
19	1.3	.60	2.01	.27	1.74	1.87	.27	1.60	240	N4	Control Film 1756-26-20 through 42
1824-2-2	1.2	1.2	1.88	.20	1.68	1.84	.25	1.59	180	N4	Control Film 1824-2-1 through 32
1756-26-12	1.0	1.2	1.90	.28	1.62	1.88	.29	1.59	120	N5	Normal 5/D7 Film
8	1.6	.08	1.54	.38	1.16	1.47	.34	1.13	240	N5, 1/2 equiv. wt.	
7	1.7	.96	2.30	.35	1.95	1.96	.44	1.52	170	N5, 2X equiv. wt.	
47	2.4	.41	1.63	.26	1.37	1.62	.27	1.35	180	N6	Low Density but Normal 5/D7 Appearance
1824-2-11	2.1	.32	2.00	.27	1.73	1.91	.31	1.60	200	N6, 1/2 equiv. wt.	
10	1.8	.70	2.26	.20	2.06	1.97	.22	1.75	160	N6, 1/2 equiv. wt.	
9	5.0	.40	2.32	.26	2.06	1.94	.28	1.66	150	N6, 2X equiv. wt.	
1756-26-6	-	-	.92	.61	.31	.93	.59	.34	140	N7	Fog and Image Very Red
1756-26-10	-	-	.45	.41	.04	.42	.39	.03	300	N8	Faint Image, Red Fog
11	-	-	.42	.42	-	.37	.37	-	60	N9	Poor Solubility; Blue Film Reaction on Mixing
7	-	-	2.25	-	-	2.00	-	-	50	N10	Film Blotched in One Pass
15	-	-	1.71	-	-	1.31	-	-	60	N10, 1/2 equiv. wt.	Film Blotched in One Pass
16	-	-	1.43	-	-	1.45	-	-	120	N10, 1/4 equiv. wt.	Faint Image Under Blotch
25	-	-	1.83	.37	1.46	1.81	.35	1.46	180	N10	I.N.D. Filter, Image with Patches of Blotch
9	-	-	.50	.45	.05	.42	.38	.04	200	N11	Faint Image, Red Fog
28	-	-	.42	.42	-	.46	.46	-	60	N12	Gray Fog
24	-	-	.75	.75	-	.70	.70	-	360	N14	No Image
8	-	-	.60	.60	-	.63	.63	-	240	N15	Reaction in Solution; Developed to Red Fog
29	-	-	-	-	-	-	-	-	360	N16	No Image or Fog Produced; Completely Dead
1824-2-12	-	-	.84	.71	.13	.79	.77	.02	300	N20	Poor Solubility; Heavy Red Fog
1756-26-30	-	-	1.41	1.41	-	1.23	1.23	-	60	N27	No Image, Dense Red Fog
1756-26-81	-	-	-	-	-	-	-	-	360	N28	Completely Dead
1756-26-37	-	-	-	-	-	-	-	-	360	N33	Slight Blue Haze
35	-	-	.85	.68	.17	.82	.64	.18	360	N34	Faint Image; Red Fog
53	-	-	1.72	.98	.74	1.88	1.09	.79	55	N36	Blue Image and Fog
1756-26-55	1.4	.70	1.55	.28	1.27	1.66	.28	1.38	58	N37	
<u>Azoxypyridine</u>											
1824-1-5	.2	.05	.47	.37	.10	.46	.41	.05	300	N17	Faint Image; Red Fog
1824-2-1	.2	.09	.46	.30	.16	.48	.30	.18	300	N18	Faint Image; Red Fog
3	.2	.09	.70	.34	.16	.76	.60	.16	280	N19	Heavy Red Fog
1824-2-6	-	-	1.30	1.30	-	1.20	1.20	-	300	N21	Poor Solubility; Red Fog
4	-	-	.29	.29	-	.30	.30	-	300	N23	Poor Solubility; Blue Fog; No Image
1824-3-6	.3	.07	.67	.52	.15	.67	.60	.07	300	N23, 0.4 equiv. wt.	Faint Image; Red Fog
1824-2-5	.4	.6	.84	.68	.16	.85	.71	.14	450	N24	Faint Image; Red Fog
<u>Alkaloid</u>											
1756-26-32	-	-	-	-	-	-	-	-	100	N29	Insoluble, Forms a Layer Over Film Preventing Fixing; No Image
1756-26-33	-	-	.15	.15	-	.24	.24	-	100	N30	Poor D260 on 4
1756-26-34	-	-	-	-	-	-	-	-	100	N31	No Image
<u>Aliphatic</u>											
1756-26-36	-	-	.18	.18	-	.27	.27	-	360	N32	Blue Fog

TABLE 2
Shelf Life Study
N-Oxides

Exp. No.	γ	AEI	Dmax B	Dmin B	Dnet B	Dmax G	Dmin G	Dnet G	ΔT_e sec.* (Tr)	ΔT_v (hr.)	N-Oxide	Comments
1824-31-13	2.2 1.3	.90 .12	1.88 .94	.19 .22	1.69 .72	- -	- -	- -	.09(36) .09(51)	0 1	Control Control 3 Steps	
15	1.8	3.5×10^{-4}	2.60	.06	2.54	-	-	-	300	0	Control	
16	1.2	1.4×10^{-4}	1.80	.07	1.73	-	-	-	300	3	Control	
1756-26-2	1.4	5×10^{-5}	1.88	.21	1.67	1.47	.21	1.26	300	0	None	Reddish Fog
3	.7	5×10^{-5}	1.33	.35	.98	1.09	.32	.77	300	3	None	Reddish Fog
4	.4	4×10^{-5}	.89	.56	.33	.75	.47	.28	300	24	None	Reddish Fog
43	-	-	2.04	.33	1.71	1.83	.29	1.59	.09(200)	0	N5	Sample Beginning to Blotch
45	-	-	1.63	1.63	-	1.54	1.54	-	.09(360)	1	N5	Completely Blotched
44	1.7	2×10^{-4}	2.24	.10	2.14	1.94	.10	1.84	300	0	N5	Normal 5/D7 Film
46	1.3	1×10^{-4}	2.04	.15	1.89	1.69	.16	1.53	300	3	N5	
47	2.4	.41	1.63	.26	1.37	1.62	.27	1.35	.09(180)	0	N6	Normal 5/D7 Film
49	-	-	1.45	1.45	-	1.34	1.34	-	.09(360)	1	N6	Blotch with No Image
48	1.2	4×10^{-4}	2.07	.09	1.98	1.85	.08	1.77	300	0	N6	
50	1.4	9×10^{-5}	1.85	.12	1.73	1.51	.11	1.40	300	3	N6	Red Background Fog
39	-	-	.86	.46	.40	.86	.42	.44	.09(240)	0	N7	Reddish Fog
41	-	-	.29	.29	-	.24	.24	-	.09(360)	1	N7	Red Fog
40	1.4	2×10^{-4}	2.27	.07	2.20	1.87	.07	1.80	300	0	N7	Normal 5/D7 Film
42	1.3	6×10^{-5}	1.65	.10	1.55	1.48	.08	1.40	300	3	N7	
1824-3-4	.33	.06	.77	.59	.18	.79	.59	.20	.09(300)	0	N18	Faint Image; High Fog
8	-	-	.75	.75	-	.78	.78	-	.09(240)	1	N18	No Image, Red Fog
5	1.4	1×10^{-4}	1.98	.07	1.91	1.77	.11	1.66	300	0	N18	
10	.9	3.5×10^{-5}	1.22	.37	.85	1.16	.34	.82	300	3	N18	Red Fog
6	.30	.07	.67	.52	.15	.67	.60	.07	.09(300)	0	N23	Heavy Fog; .44 equiv. wt.
9	-	-	.53	.53	-	.60	.50	-	.09(420)	1	N23	No Image; Red Fog
7	1.6	7×10^{-5}	2.11	.07	2.04	1.80	.10	1.70	300	0	N23	
11	1.2	4.5×10^{-5}	1.18	.12	1.06	1.08	.14	.94	300	3	N23	Slight Red Fog
1756-26-51-1	-	-	1.63	.38	1.25	1.62	.35	1.27	.09(57)	0	N34	Blotch
2	-	-	.40	.40	-	.38	.38	-	.09(120)	1	N34	No Image; Fog
52-1	1.5	2×10^{-4}	2.25	.07	2.18	1.83	.07	1.76	300	0	N34	
2	.8	6×10^{-5}	1.07	.14	.93	.90	.13	.77	300	4	N34	Slight Red Fog
53	-	-	1.72	.98	.74	1.88	1.09	.79	.09(55)	0	N36	Heavy Blue Fog Over Image
54-1	1.3	3.2×10^{-4}	2.25	.17	2.08	1.90	.19	1.17	300	0	N36	Insoluble Matter in Film
2	-	-	1.34	.10	1.24	1.25	.10	1.15	300	3	N36	Static Blotch

* ΔT_e = 300 sec.: Printout; = 0.09 sec.: exposure

TABLE 3
Dye Separation of Photolysis Dyes
1852-43

Sample Number 1845-23-n	Solution Color	TLC Visible	TLC UV	Color Residue	Effect of Light On TLC Visible	Fluorescence Spectra, Excitation	nm Emission
1	almost colorless	light yellow	bright light yellow	yellow	same	390	480
2	red	red	pink	green	same	415,420	512,518,535, 542,548
3	red	red	pink	green	lighter	398,415,420	512,525,535, 550
4	bluish purple	purple	blank	blue	lighter red	410	495
5	blue	blue	red	blue	lighter purple	422	500
6	blue	blank	red	blue	blank	398	487
7	blue	dark gray-blue	red	blue	richer blue	396	485

25X1

25X1

TABLE 4

	PHOTOGRAPH ON HAND INEQUIVALENT COATINGS	PHOTOGRAPH ON HAND	CRUDE ON HAND	LEAD TIME FOR PHOTOGRAPH FROM CRUDE
D260	11,600	(25g. 31 Dec. '71) 515 g	580 g	2 Days
CB _r ₄	2,250	(400 g) 1400	75 kg	4 Days for Freeman Immediate for Berk Ltd.
P.O.	6,200	(20 g) 55 g	200 g	4 Days
D7	12,300	(500 g) 350 g	UNLTD.	2 Days
POLYSTYRENE	100 k	50 kg	UNLTD.	IMMEDIATE
BENZENE	25 k	50 Liters	UNLTD.	IMMEDIATE

MATERIALS INVENTORY

30 JUNE 1972

FORMULA 5/D7

TABLE 5

D260 BALANCE SHEET

5 kg Contract (\$3,750) for Crude D260
from ChemSampCo., dated late 1971.

3,700 g	Delivered to Date
- 500	Delivered in 1971
<hr/> 3,200	Delivered 1 January to 30 June '72
- 1,020	Crude On Hand
<hr/> 2,180	
× 40%	Average Yield (70% Now)
<hr/> 870	Photograde D260 Produced
- 100	Photograde Reject on Hand
<hr/> 770	Photograde Accepted
180	Hand Coating
50	Synthesis Work
15	Retain Samples
10	Nine (9) Shipments East
<hr/> - 255	Total Consumed
<hr/> <hr/> 515	PHOTOGRADE ON HAND

TABLE 6

STATUS OF QC TESTS FORMULA 5/D7 INGREDIENTS

All Still Require Film Coating Test For Final Approval

D260 (ChemSampCo, \$1,200/kg)

Contaminants	Test
TMB	TLC
Anthrone of D260	TLC/UV < 10 ppb
DMAP	Test for Anthrone
Condensation Product Possible	Identification Work Underway
Others	
Purification (70% Yield)	
Dry Column Chromatography	
Recrystallization	

TABLE 7
STATUS OF QC TESTS

D7 (MCB Co., \$50/kg for Starting Materials)

Only Trace Impurities After First Recrystallization

No Apparent Deleterious Effect

No Identification Attempted

No Additional Purification

4PO (EK, MCB; \$75/kg for Crude)

Only Trace Impurities in Crude

No Consistent Deleterious Effect

No Identification Attempted

Purification; Recrystallization Plus Three Days Drying

CB₄ (Freeman, BDH, Berk Ltd., \$2.45/kg for Crude)

Contaminant: Hexabromoethane

Effect probably depends on grade of D260

Test: TLC/D260 Spray

Purification: Recrystallization or Sublimation

TABLE 8

COMPARISON OF CONTROLS and P. E.'s RESULTS

Shipment Number	Exposure Sec.	M. C.	RLD Sec.	AEI	γ	Dmax	Densitometer TD-102
Red Lite Developed:							
7	10	120**	45	1.1×10^{-3}	14.3	2	Perkin Elmer
7	10	120	60	2.2×10^{-3}	9.5	2	Perkin Elmer
7	10	120	75	8.7×10^{-3}	26.4	2	Perkin Elmer
8*	10	120	45	2.3×10^{-3}	6.8	2.4	<input type="text"/>
*8, Control	.088	220	40	0.65	2.0	1.95	<input type="text"/>
7, Control	.09	188	49	1.4	3.8	2.5	<input type="text"/>
Printout:							
7, Control	300	188	-	2.2×10^{-4}	1.8	2.5	<input type="text"/>
7	180	120	-	2.4×10^{-4}			Perkin Elmer
*8, Control	300	220	-	1.8×10^{-4}	1.8	2.4	<input type="text"/>
8, Control	300	220	-	0.9×10^{-4}	2.1	2.6	<input type="text"/>
*8	180	120	-	2.6×10^{-4}	1.3	2	<input type="text"/>

Controls were exposed and processed All others were exposed and processed at Perkin Elmer.

* These are plotted in Figure 31

** 120 m. c. is the value currently estimated to have been correct. 289 m. c. was the value used at the time of the April visit.